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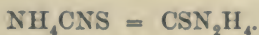
JOURNAL  
OF  
THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*A Study of the Dynamic Isomerism of Thiourea and Ammonium Thiocyanate. The Volumetric Determination of Thiourea by means of Iodine.*

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S., and EMIL A. WERNER, F.I.C.

THE method of producing thiourea for use in the arts is that by which one of us succeeded in isolating the substance in 1868 (this Journal, 21, 1). This consists in carefully heating fused ammonium thiocyanate so as to secure as far as possible the molecular rearrangement represented by the expression



It was early noticed that this change was very partial, and it was also found that pure thiourea, when fused, reverted to a considerable extent to ammonium thiocyanate; that is to say, the action is in some degree reversible. At the time the substance was discovered, it seemed much less important to study the extent of the conversion of thiocyanate into thiourea than to examine the latter and investigate the very large number of derivatives it afforded. However, while this work was in progress, other chemists—notably Volhard (*Ber.*, 1873, 6, 92)—sought to ascertain the largest proportion of thiourea produced at a single operation, and obtained as a maximum about 22 per cent. of the thiocyanate taken for experiment. Other estimates varied between 16 and 20 per cent., probably owing to the use of small quantities of impure and moist thiocyanate in the first instance.

Again, the estimates varied considerably as to the extent of reversion on fusing pure thiourea. Volhard (*loc. cit.*) considered that about 66 per cent. reverted to ammonium thiocyanate; but, more recently, Waddell (*J. Physical Chem.*, 1898, 2, 525) found that equilibrium is reached from either side at 152–160°, when the ratio of thiourea to thiocyanate is 21.2 to 78.8. Waddell's experiments, though well-conceived, were carried out with small quantities, usually one gram, of admittedly somewhat impure materials, and were further affected by the use of Volhard's unsatisfactory method of estimating thiourea by silver nitrate in presence of excess of ammonia.

This case of "balanced action," apparently conditioned by heat alone, is cited by Lowry (*Trans.*, 1899, 75, 235) as an example of what he terms "dynamic isomerism."

Having to review this question of yield of thiourea for practical purposes, we decided to make a systematic study of the changes on a comparatively large scale. The results of this inquiry we beg to lay before the Society, as they are essentially different from those of previous observers.

The method we adopted was to heat a kilogram of carefully dried ammonium thiocyanate in a large beaker well immersed in a bath of glycerol. The temperature was raised as quickly as possible to the melting point of the salt (148–149°), and two thermometers were fixed in position so that the bulb of one was near to the bottom of the beaker and that of the other well under the surface of the fused material, which was kept in motion by a stirrer. The temperature of the liquid was then rapidly raised to the desired point and maintained as equable as possible. A number of dip tubes were provided, so that 12–14 grams of material could be removed from the liquid at equal time intervals and have their contents suddenly chilled and solidified. Ten grams of each specimen so obtained were dissolved in 500 c.c. of water for the determination of the percentage of thiourea present in the fused mass at the time the sample was taken. The method of analysis employed, which presents several points of interest, is described on p. 7, and depends on the perfectly regular action of iodine on thiourea, even in presence of a large excess of thiocyanate, provided that the solutions are sufficiently dilute and acid.

Two main series of experiments were made on this plan.

*Series I.*—In this, the temperature was quickly raised to 170°, and the first portion was then taken for analysis. At this nearly constant temperature, samples were removed at 5 minute intervals throughout the operation, which lasted 60 minutes.

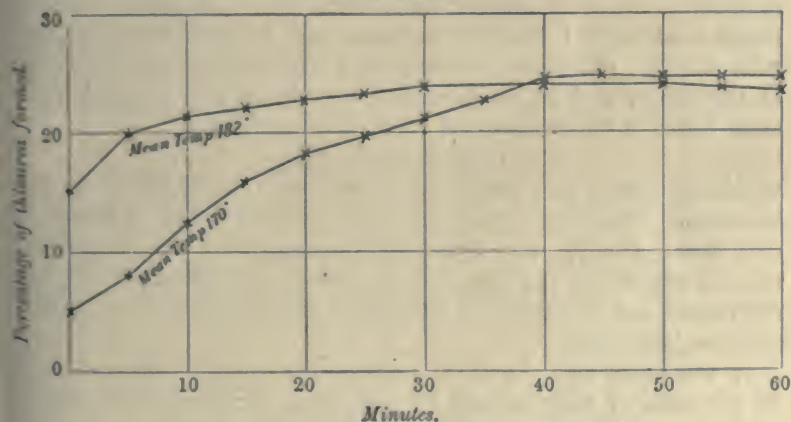
*Series II.*—The average temperature in this series was 182°, and portions were taken for analysis at 5 minute intervals.

The results of both series are given in Table I, from which Curve I has been plotted :

TABLE I.

| Time in minutes. | Percentages of thiourea formed. |                        | Time in minutes. | Percentages of thiourea formed. |                        |
|------------------|---------------------------------|------------------------|------------------|---------------------------------|------------------------|
|                  | Mean $t=170^{\circ}$ .          | Mean $t=182^{\circ}$ . |                  | Mean $t=170^{\circ}$ .          | Mean $t=182^{\circ}$ . |
| 0                | 5.22                            | 15.30                  | 35               | 22.80                           | —                      |
| 5                | 7.90                            | 20.00                  | 40               | 24.32                           | 23.94                  |
| 10               | 12.82                           | 21.28                  | 45               | 24.76                           | —                      |
| 15               | 15.96                           | 22.04                  | 50               | 24.32                           | 23.56                  |
| 20               | 18.24                           | 22.42                  | 55               | 24.30                           | 23.18                  |
| 25               | 19.76                           | 22.80                  | 60               | 24.30                           | —                      |
| 30               | 21.66                           | 23.18                  |                  |                                 |                        |

CURVE I.



It was found to be useless to operate at higher temperatures than  $182^{\circ}$ , as both isomerides then decomposed, guanidine thiocyanate, ammonium trithiocarbonate, and other products being rapidly formed. On the other hand, ammonium thiocyanate retained just at its melting point ( $148-149^{\circ}$ ), changed very slowly, and gave only 15.2 per cent. of thiourea, even after 40 minutes.

It is clear from the results of the two main series of experiments that:

1. The maximum proportion of thiourea formed at a single operation\* by heating ammonium thiocyanate was 24.76 per cent.

\* We have obtained a yield of 43 per cent. by dissolving the product in water, separating by crystallisation the crude thiourea, evaporating the mother liquors to dryness, again fusing, and repeating the treatment several times.

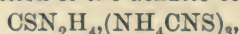


2. The maximum was reached after 45 minutes at a temperature of  $170^{\circ}$ ; but at  $182^{\circ}$  the change was more rapid in the earlier stages, though the time required for the maximum effect was nearly the same as before, and decomposition then proceeded more rapidly.

The reverse change of pure thiourea into ammonium thiocyanate was next examined.

A quantity of pure and dry thiourea was heated until it completely melted ( $159^{\circ}$ ); a 10 gram sample was suddenly cooled and was found to contain 28.8 per cent. of ammonium thiocyanate. The temperature was then raised to  $170^{\circ}$ , and we found 74.2 per cent. of ammonium thiocyanate after 45 minutes. The temperature was maintained for 20 minutes longer, but the proportion was practically unaltered.

Therefore, when pure and dry materials were used in the first instance, equilibrium was reached from either side when the isomerides were present in the fused mass in the proportions which are, substantially, 25 per cent. of thiourea and 75 per cent. of ammonium thiocyanate. In other words, equilibrium was established when the liquid contained 1 mol. of thiourea and 3 mols. of ammonium thiocyanate. It seemed probable that the complete arrest of change at this stage, and at temperatures very favourable to its continuance, is due to the formation of the definite compound



which is more stable under the conditions than either of its constituents. A large mass of the product, when allowed to cool down slowly, was found to include about its centre well-marked crystalline aggregates of the above composition. The following results and the study of the action of solvents tend to confirm the view just stated.

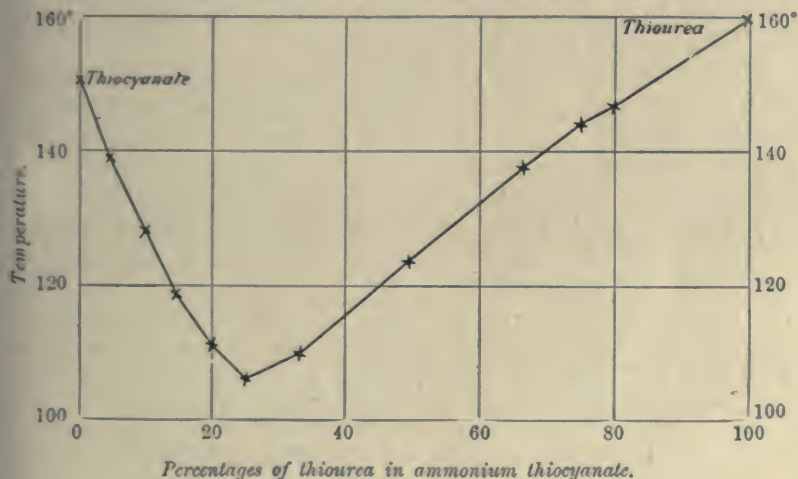
It was noted that the fused mass, which contained approximately 25 per cent. of thiourea and 75 per cent. of thiocyanate, did not solidify until the temperature fell to  $105$ — $106^{\circ}$ . The two isomerides, being perfectly miscible liquids when fused, were certain to afford eutectic mixtures, and the question arose whether the melting point of the 1 : 3-compound is also the eutectic point.

In order to settle this question, we made a number of very intimate mixtures of pure thiourea and ammonium thiocyanate, and determined their points of complete liquefaction, so as to avoid, as far as practicable, the complication due to intramolecular change. The results are stated in Table II, and are graphically shown on the annexed Curve II, from which it is obvious that the experimental answer is in the affirmative.

TABLE II.

| Composition of mixtures. |                       | Temperatures of complete liquefaction. | Composition of mixtures. |                       | Temperatures of complete liquefaction. |
|--------------------------|-----------------------|--|--------------------------|-----------------------|--|
| Thiurea per cent.        | Thiocyanate per cent. |  | Thiurea per cent.        | Thiocyanate per cent. |  |
| 0                        | 100                   | 148°                                   | 33·3                     | 66·6                  | 110°                                   |
| 5                        | 95                    | 137                                    | 50                       | 50                    | 124                                    |
| 10                       | 90                    | 128                                    | 66·6                     | 33·3                  | 139                                    |
| 15                       | 85                    | 118                                    | 75                       | 25                    | 144                                    |
| 20                       | 80                    | 111                                    | 80                       | 20                    | 147                                    |
| 25                       | 75                    | 106                                    | 100                      | 0                     | 159                                    |

CURVE II.—Relations of melting points to composition.



*Action of Solvents.*—When the previously fused material which contains thiourea and thiocyanate in the ratio of 1 to 3 was warmed with insufficient acetone to dissolve it completely and the solution cooled, fine, feathery groups of silky needles separated. These crystals, which were quite distinct in appearance from either isomeride when crystallised from acetone, gave 51·5 per cent. of thiourea, and therefore consisted of  $\text{CSN}_2\text{H}_4\cdot\text{NH}_4\text{CNS}$ . Theory requires 50 per cent., but the crystals could not be farther purified from inevitable excess of thiocyanate as they were wholly dissociated by re-solution.

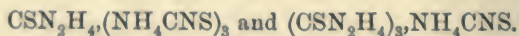
With alcohol, even when nearly anhydrous, the change proceeds farther and the compound  $(\text{CSN}_2\text{H}_4)_3\cdot\text{NH}_4\text{CNS}$  can be crystallised

from the solution. The same compound can, however, be easily obtained, and in a state of greater purity, by dissolving the fused product in rather more than its own weight of hot water, and allowing the solution to cool slowly. Fine groups of long, tapering prisms having a satin-like lustre crystallise out. These bear repeated washing with ice-cold water and pressing with bibulous paper between each washing. When once dried, they can be exposed to the air freely without absorbing moisture, indicating the absence of free ammonium thiocyanate. If redissolved in water, complete separation of the isomerides occurs. Crystals purified as described gave 74.48 per cent. of thiourea, the rest being combined thiocyanate (calc., 75 per cent. thiourea). The crystals melt at  $144^{\circ}$ , but since the thiourea present gradually reverts, when fused, to ammonium thiocyanate, the point of resolidification is lower.

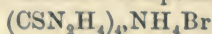
In a fine specimen of these large groups of crystals, prepared some 33 years ago, the satin-like lustre is still retained, and the crystals have merely assumed a slightly brownish colour. On analysis, these afforded us exactly 75 per cent. of thiourea.

Hintze (*Jahresber. Chem.*, 1884, 462), Carrara (*Gazzetta*, 1892, 22, i, 343), and others have obtained similar crystals to those just described, but they regarded them as those of the compound,  $\text{CSN}_2\text{H}_4\cdot\text{NH}_4\text{CNS}$ , possibly owing to the difficulty in removing adherent thiocyanate.

It is evident, from the results recorded in this paper, that the state of equilibrium reached when either ammonium thiocyanate or thiourea is heated at  $170^{\circ}$  for some 45 minutes is conditioned as much by perfectly definite chemical attraction as by heat. It is farther seen that the relative attractions of the saline and non-saline isomerides at comparatively high temperatures are reversed at low temperatures with more or less dissociation in presence of solvents, hence, under the respective conditions, we have the complementary compounds



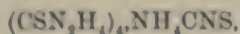
Some years ago (*Trans.*, 1891, 59, 384), one of us made known the existence of a number of thiourea compounds of which



may be taken as a type. At that time we sought to replace the ammonium bromide in the above by the thiocyanate, but without success, as we operated in the presence of solvents. We now find that the compound is easily produced when the perfectly dry materials are mixed first in the form of fine powder and the mixture is carefully fused, and then quickly cooled. When dissolved in nearly anhydrous alcohol a few crystals of thiourea separate at first, and then a felted mass of long, thin needles resembling the ammonium bromide compound. These were slightly yellow in colour, and after



purification by repeated washing with cold alcohol gave 78·87 per cent. of thiourea, according fairly with the formula



Previous fusion of the materials together was, therefore, more efficient in determining combination of the kind required than merely heating in the solvent.

#### *Volumetric Determination of Thiourea by means of Iodine.*

Volhard's volumetric method of estimating thiourea (*loc. cit.*) depends on the desulphuration of the latter, with formation of cyanamide, by the action of silver nitrate in presence of excess of ammonia. This method is fairly satisfactory in nearly pure solutions of thiourea, but its author admits that its results are irregular when much ammonium thiocyanate is present. In preparing for the work recorded in the foregoing paper, we therefore sought to devise a method capable of giving reliable results, even when the thiocyanate is in large excess and we found that this end could be attained by means of iodine if used under the special conditions we shall describe.

When iodine solution is added to thiourea dissolved in a small proportion of water, the colour of the halogen disappears until a state of equilibrium is reached; the condition is disturbed by further dilution, and the liquid decolorises more iodine. This is, therefore, a reversible action, like so many others in which iodine is concerned, and can be made perfectly regular, as in other cases, by large dilution. In presence of a sufficient volume of water, we found that 0·76 gram of thiourea required 1·268 of iodine, or 1 mol. of the former to 1 at. of the latter. The dilution required is such that the liquid titrated shall not contain more than 0·05 gram of thiourea in 250 c.c., and the action proceeds most regularly in presence of some free sulphuric acid. The iodine solution used is deci- or centi-normal. Under these conditions, we found that the addition of successive quantities of ammonium thiocyanate did not commence to affect the determinations of thiourea until at least 16 mols. of thiocyanate were added for 1 mol. of thiourea.

The method as applied to one of the fusion products of ammonium thiocyanate was as follows:

Ten grams of the material were dissolved in 500 c.c. of water. Ten c.c. of this solution were diluted with 250 c.c. of water, and 5 c.c. of diluted sulphuric acid (1 to 7) added with 2 c.c. of a fresh starch solution, and iodine standard solution was then added as required. Before the end is reached, the liquid acquires a *lavender* tint, but this is easily distinguished in full daylight from the pure blue colour

developed by 1/20th c.c. of the standard iodine marking the final action.

The investigation of the exact nature of the change involved in the above process was in progress, together with re-examination of the results of Claus (*Annalen*, 1875, 179, 139), McGowan (*Trans.*, 1886, 49, 195), and Storch (*Monatsh.*, 1890, 11, 452) on the action of iodine on thiourea under various conditions, when we found that the subject was also being examined by Dr. Hugh Marshall (*Proc. Roy. Soc. Edin.*, 1902, 24, 233). We have therefore not proceeded farther, but so far as our results went they indicated that iodine acts, in our volumetric method, by removing one atom of hydrogen as hydriodic acid from each molecule of thiourea.

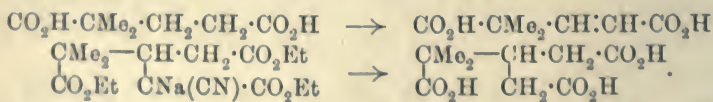
UNIVERSITY LABORATORY,  
TRINITY COLLEGE, DUBLIN.

## II.—*The Synthesis of αα-Dimethylglutaric Acid, of β-Hydroxy-αα-dimethylglutaric Acid, and of the cis- and trans-Modifications of αα-Dimethylglutaconic Acid.*

By W. H. PERKIN, jun., and ALICE E. SMITH, B.Sc. (1851 Exhibition Scholar of University College, Bangor).

IN a paper published a short time since (*Trans.*, 1902, 81, 246), it was shown that *isocamphoronic acid* may be readily synthesised with the aid of the following series of reactions.

*αα*-Dimethylglutaric acid is first converted into *αα*-dimethylglutaconic acid, and the ester of the latter acid condensed with the sodium compound of ethyl cyanoacetate; the compound thus produced, when hydrolysed with sulphuric acid, yields *isocamphoronic acid*:

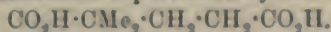


The only unsatisfactory point in this synthesis is the fact that the dimethylglutaric acid, which is the foundation of the whole process, had to be prepared by the oxidation of *isolaunonic acid*, since no other method was known by which it could be readily obtained.

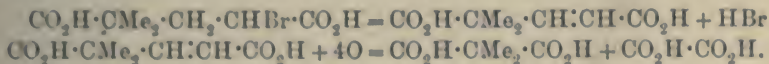
That the acid employed in the synthesis is *αα*-dimethylglutaric acid is proved by the fact that, on oxidation with nitric acid, it yields *αα*-dimethylsuccinic acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , and since it is



isomeric with ββ-dimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , it must have the constitution represented by the formula

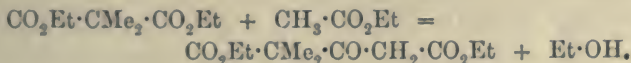


In further support of this formula is the fact that, on treatment with bromine and subsequent hydrolysis, it is converted into αα-dimethylglutaconic acid (m. p.  $172^\circ$ ), the constitution of which is proved by the fact that, on oxidation, it yields dimethylmalonic acid and oxalic acid:

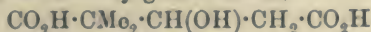


So far, however, no satisfactory synthesis of αα-dimethylglutaric acid has been described, although Montemartini (*Gazzetta*, 1898, 28, ii, 290) claims to have obtained this acid in small quantities by the following series of reactions. Ethyl isobutylacetate was first treated with chlorine, and the ethyl monochloroisobutylacetate thus obtained was digested with potassium cyanide and the product hydrolysed. Since the resulting acid yielded an anilic acid which melted at  $145\cdot5^\circ$ , Montemartini concluded that it was αα-dimethylglutaric acid.

In the present communication, we describe a synthesis of αα-dimethylglutaric acid from simple materials, which, although it gives only a small yield of this acid, nevertheless leaves no doubt as to its constitution. When sodium acts on a mixture of ethyl dimethylmalonate and ethyl acetate, condensation takes place readily, with the formation of ethyl αα-dimethylacetonedicarboxylate:



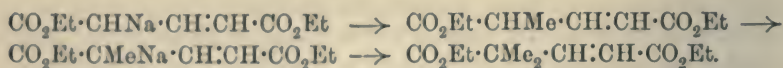
This ester, which boils at  $185\text{--}190^\circ$  under 100 mm. pressure, had not previously been prepared; it is isomeric with the ethyl αγ-dimethylacetonedicarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , which Dünschmann and Pechmann (*Annalen*, 1891, 261, 182) obtained by treating ethyl acetonedicarboxylate with methyl iodide and sodium methoxide, and which boils at practically the same temperature, namely,  $190\text{--}200^\circ$  under 130 mm. pressure. When the new ester is reduced with sodium amalgam and afterwards with hydriodic acid under the conditions described in the experimental part of this paper, it yields β-hydroxy-αα-dimethylglutaric acid,



(m. p.  $158\text{--}160^\circ$ ), and αα-dimethylglutaric acid.

Besides leading to a synthesis of αα-dimethylglutaric acid, this research has given results which, we think, throw much light on the difficult question of the nature of the αα-dimethylglutaconic acids,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ . Henrich (*Monatsh.*, 1899, 20, 560) first

prepared a readily soluble acid of this constitution by treating ethyl glutaconate with sodium methoxide and methyl iodide, thus:



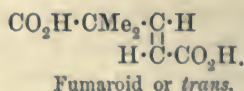
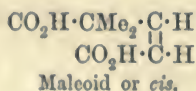
The acid obtained on hydrolysing the product softened at  $123^\circ$  and began to melt at  $126^\circ$ ; at  $129\text{--}130^\circ$ , most of it melted, but the fused mass did not become clear until  $133^\circ$ . This description is important, in view of the work discussed in this paper, and it should be said at once that there can be no doubt that Henrich's acid was an *aa*-dimethylglutaconic acid, because of the fact that on oxidation with permanganate it yielded dimethylmalonic acid.

About the same time, Conrad (*Ber.*, 1899, 32, 137; 1900, 33, 1921), by a complicated series of reactions, prepared an acid melting at  $150^\circ$ , which he called *aa*-dimethylglutaconic acid, but the identity of which he did not prove by examining its behaviour on oxidation with permanganate. This synthesis of Conrad's need not be further discussed, since, in a previous paper (Perkin, *Trans.*, 1902, 81, 249), reasons are given which make it appear very doubtful whether the acid has the constitution assigned to it by Conrad.

Subsequently, a well characterised and sparingly soluble *aa*-dimethylglutaconic acid melting at  $172^\circ$  was prepared by one of us (Perkin, *loc. cit.*, p. 253) by the hydrolysis of ethyl  $\gamma$ -bromo-*aa*-dimethylglutarate with alcoholic potash.

$\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et} \longrightarrow \text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .  
On oxidation with permanganate, this acid was converted into dimethylmalonic acid and oxalic acid; there can therefore be no doubt as to its identity.

If the formula of *aa*-dimethylglutaconic acid is examined, it will be seen that an acid of this constitution should exist in *cis*- and *trans*-modifications corresponding to maleic and fumaric acids:



When the acid of melting point  $172^\circ$  was discovered, it was suggested (*loc. cit.*, p. 250) that its high melting point, sparing solubility in water, and incapability of forming an anhydride, as well as the fact that it is not easily attacked by bromine, pointed to its being the *trans*-modification, and this view is confirmed by the results given below. During the course of the present investigation, it was found that one of the products of the reduction of *aa*-dimethylacetonedicarboxylate,

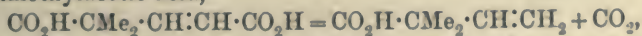
when isolated under the conditions described in the experimental part of this paper, is an αα-dimethylglutaconic acid which melts sharply at 134—135°. Since this acid is isomeric with the acid of melting point 172° and its formation from ethyl αα-dimethylacetonedicarboxylate allows of no doubt as to its constitution, it must evidently be the *cis*-modification figured above. The properties of the acid entirely support this view. The only matter which remains still to be investigated in order to make the relationship between the *cis*- and *trans*-acids perfectly clear is the determination of the conditions under which each isomeride may be converted into the other, and this we propose to undertake in the near future.

That the acid synthesised by Henrich, which melted approximately at 130°, consisted mainly of *cis*-dimethylglutaconic acid was now almost a matter of certainty, and, indeed, experiments which were carried out in these laboratories with a specimen of the acid prepared exactly according to Henrich's instructions afford almost conclusive evidence on this point.

Dr. W. T. Lawrence, who conducted these experiments, first confirmed Henrich's statement that the acid, on oxidation, gives dimethylmalonic acid, and then by submitting it to a long series of fractional crystallisations succeeded in separating from it an acid melting at 135° which is evidently identical with the *cis*-acid described in this paper. At the same time, a small quantity of a sparingly soluble acid was isolated which melted at about 159°, and very probably consisted of impure *trans*-acid.

A further interesting observation was made during the course of the present investigation, namely, that the β-hydroxy-αα-dimethylglutaric acid, which is the direct product of the reduction of ethyl αα-dimethylacetonedicarboxylate, may be converted into *trans*-αα-dimethylglutaconic acid in two different ways.

When the hydroxy-acid is rapidly distilled under reduced pressure, the distillate is semi-solid and yields on crystallisation small quantities of the *trans*-acid melting at 172°. In the previous paper, of which mention has already been made (*loc. cit.*, p. 256), it was shown that this acid, when slowly heated, is decomposed into carbon dioxide and vinyl dimethylacetic acid,



but these later experiments prove that it may, under certain conditions and like fumaric acid, distil unchanged.

The second method, by which an almost quantitative conversion into *trans*-αα-dimethylglutaconic acid may be brought about, consists in treating the hydroxydimethylglutaric acid with phosphorus pentachloride, decomposing the product with alcohol, and hydrolysing



the ethyl  $\beta$ -chloro- $\alpha\alpha$ -dimethylglutarate thus produced with alcoholic potash:



#### EXPERIMENTAL.

*Ethyl  $\alpha\alpha$ -Dimethylacetonedicarboxylate*,  $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ .

In preparing this substance, sodium (23 grams) was melted in a thick flask under boiling toluene, the flask wrapped in a cloth, and violently agitated in order to bring the sodium into the finest possible condition. The toluene was removed as far as possible by decantation, and then a mixture of ethyl dimethylmalonate (63 grams) and ethyl acetate (60 grams, carefully dried) added in small quantities at a time, any considerable rise of temperature being checked by cooling with water.

The flask was connected with a reflux apparatus and allowed to stand until the reaction slackened, and afterwards heated for about 6 hours, first on the water-bath and then in a salt-bath, the last traces of sodium being removed by adding further small quantities of ethyl acetate. The dark brown product was mixed with dilute hydrochloric acid, extracted with ether, the ethereal solution washed with water until free from alcohol, dried over calcium chloride, evaporated, and the residual oil fractionated. As soon as the excess of ethyl acetate had been removed, the distilling flask was connected with the vacuum fractionating apparatus and the distillation continued under 100 mm. pressure. A quantity of ethyl acetoacetate and unchanged ethyl dimethylmalonate first passed over, and then a dark oil distilled, which, after repeated fractionation, boiled constantly at  $185\text{--}190^\circ$  under 100 mm. pressure and gave, on analysis, the following results:

0.1541 gave 0.3248  $\text{CO}_2$  and 0.1107  $\text{H}_2\text{O}$ . C = 57.5; H = 8.0.

0.1233 „ 0.2591  $\text{CO}_2$  „ 0.0883  $\text{H}_2\text{O}$ . C = 57.4; H = 7.9

$\text{C}_{11}\text{H}_{13}\text{O}_5$  requires C = 57.4; H = 7.8 per cent.

Ethyl dimethylacetonedicarboxylate is an almost colourless oil, the alcoholic solution of which gives with ferric chloride an intense reddish-violet coloration.

*Reduction of Ethyl  $\alpha\alpha$ -Dimethylacetonedicarboxylate. Formation of  $\alpha\alpha$ -Dimethylglutaric Acid,  $\beta$ -Hydroxy- $\alpha\alpha$ -dimethylglutaric Acid, and cis- $\alpha\alpha$ -Dimethylglutaconic Acid.*

Our first experiments on the reduction of ethyl dimethylacetonedicarboxylate were carried out by dissolving the ester in dilute alcohol and treating the solution in flat basins with sodium amalgam, no

attempt being made to neutralise the alkali as it was formed. Under these conditions, however, the ester is almost completely hydrolysed and converted into dimethylmalonic acid and acetic acid.

The reduction was finally carried out successfully by dissolving the ester (10 grams) in alcohol (100 c.c.), adding an equal volume of water, and treating the solution with sodium amalgam in a porcelain beaker, a rapid stream of carbon dioxide being passed through and the mixture kept thoroughly stirred with a mechanical stirrer and well cooled during the whole operation. The amalgam was added in small quantities at a time until a sample of the product, when extracted with ether, no longer yielded an oil giving a violet coloration with ferric chloride; this was usually the case at the end of 2 days. The mixture was then diluted with water, separated from the mercury, acidified with hydrochloric acid, evaporated to dryness, and the residue ground up with sand and extracted in a Soxhlet apparatus with alcohol. On removing the alcohol by evaporation on the water-bath, a dark brown oil was obtained, which, even after standing for some days in a vacuum desiccator, showed no signs of crystallising.

The oil (5 grams) was then digested with hydriodic acid (25 c.c. of sp. gr. 1·96) and amorphous phosphorus (1 gram) for 4 hours, when, on extracting with ether, washing the ethereal solution with bisulphite to remove iodine, and distilling off the ether, a brown oil was obtained, which, after standing for some days in an exhausted desiccator over sulphuric acid, deposited a quantity of crystals.

In contact with porous porcelain, the dark oil was soon absorbed. The residual, yellowish mass of crystals was dissolved in water and the solution digested with purified animal charcoal and concentrated, when, on cooling, colourless, glistening prisms separated which melted at 90°. On analysis:

0·1521 gave 0·2943 CO<sub>2</sub> and 0·1041 H<sub>2</sub>O. C=52·8; H=7·6.

0·1674 „ 0·3212 CO<sub>2</sub> „ 0·1144 H<sub>2</sub>O. C=52·4; H=7·6.

C<sub>7</sub>H<sub>12</sub>O<sub>4</sub> requires C=52·5; H=7·5 per cent.

This acid is αα-dimethylglutaric acid, although the observed melting point is somewhat higher than that usually assigned to it.

Tiemann (*Ber.*, 1895, 28, 2176), who prepared this acid by the oxidation of β-campholenic acid, gives the melting point as 85°, and Blanc (*Bull. Soc. chim.*, 1898, [iii], 19, 284) and Perkin (*Trans.*, 1898, 73, 847), who both obtained the acid from isolaunonic acid by oxidation, also observed the melting point 85°. In order, therefore, to be certain of the identity of the synthetical acid, it was converted, by boiling with acetic anhydride, into the anhydride, and from this, by treatment with aniline, the anilic acid was prepared; the latter melted at 144°, which is the melting point of the anilic acid of αα-dimethyl-

glutaric acid. Moreover, on mixing a small quantity of the synthetical acid with an equal amount of a specimen of the acid which had been prepared from isolauronic acid, the mixture melted at 87—90°. There can therefore be no doubt that the synthetical acid is *αα*-dimethylglutaric acid, and it is probable that the melting point of this acid, when pure, is 90° and not 85°.

The porous porcelain which had been used to absorb the brown oil in the purification of the crude dimethylglutaric acid, as explained above, was broken up and extracted in a Soxhlet apparatus with ether. The extract was evaporated, but the residual dark brown oil did not show any signs of crystallising, even after standing for a week in a vacuum desiccator. It was boiled with much water, filtered from a small quantity of insoluble matter, and the filtrate, after decolorising with purified animal charcoal, again extracted with ether. The ethereal solution was dried over calcium chloride and evaporated when the syrupy residue, which was now much lighter in colour, gradually deposited crystals and became semi-solid. On rubbing the mass with dry ether, the oily impurity dissolved, leaving a crystalline residue, which was collected on the pump and rapidly washed with the same solvent. The ochre-coloured residue was dissolved in dilute sodium carbonate, digested with animal charcoal, filtered, and the filtrate acidified with hydrochloric acid, when, on standing, large, colourless prisms like sugar crystals gradually separated. These were collected, recrystallised from water, and consisted then of pure  $\beta$ -hydroxy-*αα*-dimethylglutaric acid, as the following analyses and examination of properties show :

0.1860 gave 0.3248 CO<sub>2</sub> and 0.1144 H<sub>2</sub>O. C = 47.6 ; H = 6.8.

0.1694 „ 0.2948 CO<sub>2</sub> „ 0.1041 H<sub>2</sub>O. C = 47.4 ; H = 6.8.

C<sub>7</sub>H<sub>12</sub>O<sub>5</sub> requires C = 47.8 ; H = 6.8 per cent.

0.1898 gram dissolved in water required for neutralisation 0.0864 gram of NaOH, which is exactly the amount required for a dibasic acid C<sub>7</sub>H<sub>12</sub>O<sub>5</sub>.

$\beta$ -Hydroxy-*αα*-dimethylglutaric acid melts at 158—160° and is readily soluble in water or alcohol, but sparingly so in dry ether, benzene, or light petroleum. Its behaviour on distillation and when treated with phosphorus pentachloride is described in the next section. This hydroxy-acid is apparently new and is isomeric with  $\gamma$ -hydroxy-*αα*-dimethylglutaric acid, CO<sub>2</sub>H·CMe<sub>2</sub>·CH<sub>2</sub>·CH(OH)·CO<sub>2</sub>H, which Perkin (Trans., 1902, 81, 259) obtained in the form of its lactone by the hydrolysis of ethyl  $\gamma$ -bromo-*αα*-dimethylglutarate with potash.

The ethereal mother liquors of the hydroxy-acid were evaporated and the dark oily residue digested with acetic anhydride for two hours and then fractionated, when a considerable fraction distilling at



170—190° under 70 mm. pressure was obtained, and on redistillation the bulk of this passed over at 180—185° under 75 mm. pressure, which is the boiling point of the anhydride of  $\alpha\alpha$ -dimethylglutaric acid. As, however, the oil did not solidify, even when cooled to  $-10^\circ$ , it was mixed with excess of a filtered solution of potash in methyl alcohol when, almost immediately, a quantity of a crystalline, sparingly soluble potassium salt separated. This was collected on the pump, washed with methyl alcohol, dissolved in water, boiled until free from methyl alcohol, acidified, and the clear solution extracted five times with ether.

The ethereal solution, after drying over calcium chloride, deposited on evaporation a colourless oil which rapidly solidified, the crystalline mass melting at about  $130^\circ$ . This was dissolved in a little water and the solution saturated with hydrogen chloride when, after two days, long, colourless needles had separated together with a very small quantity of a substance crystallising in brown warts.

The needles were mechanically separated and again crystallised from hydrochloric acid, after which they melted at  $135$ — $137^\circ$  and consisted of pure *cis*- $\alpha\alpha$ -dimethylglutaconic acid. On analysis:

0.1018 gave 0.1992  $\text{CO}_2$  and 0.0592  $\text{H}_2\text{O}$ .  $\text{C} = 53.4$ ;  $\text{H} = 6.4$ .

$\text{C}_7\text{H}_{10}\text{O}_4$  requires  $\text{C} = 53.2$ ;  $\text{H} = 6.3$  per cent.

0.0871 gram required for neutralisation 0.0448  $\text{NaOH}$ , whereas this amount of a dibasic acid  $\text{C}_7\text{H}_{10}\text{O}_4$  should neutralise 0.0441  $\text{NaOH}$ .

The *cis*-acid is very soluble in water and most organic solvents, but it is sparingly soluble in hydrochloric acid. Its solution in sodium carbonate rapidly decolorises permanganate, showing that it is an unsaturated acid.

*cis*-Dimethylglutaconanilic Acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  (1).—When the *cis*-acid is heated with acetic anhydride in a test-tube for 10 minutes and the acetic acid and excess of acetic anhydride driven off by heating at  $180^\circ$  and passing a current of dry air, an oil remains which undoubtedly consists of the anhydride of the *cis*-acid. No attempt was, however, made to purify this, owing to the small amount at our disposal. The crude anhydride dissolves readily in benzene, and on the addition of aniline, a considerable rise of temperature takes place, and in a short time crystallisation sets in and the whole soon becomes a semi-solid mass.

The crystals were collected on the pump, left in contact with a porous plate to remove oily mother liquor, and then crystallised from dilute alcohol, from which the anilic acid separated in colourless needles melting at about  $164^\circ$  with decomposition. On analysis:

0.1449 gave 0.3540  $\text{CO}_2$  and 0.0876  $\text{H}_2\text{O}$ .  $\text{C} = 66.6$ ;  $\text{H} = 6.7$ .

0.1754 gave 9.2 c.c. nitrogen at  $19^\circ$  and 758 mm.  $\text{N} = 6.0$ .

$\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$  requires  $\text{C} = 66.9$ ;  $\text{H} = 6.4$ ;  $\text{N} = 6.0$  per cent.

*cis*- $\beta$ -Dibromo- $\alpha\alpha$ -dimethylglutaric Acid,

—When *cis*-dimethylglutaconic acid is thinly spread out on a watch-glass and exposed to the vapour of bromine, it is soon converted into a brown liquid and if, after standing for 2 hours, the watch-glass is transferred to a vacuum desiccator containing powdered potash, the excess of bromine and traces of hydrogen bromide rapidly evaporate, leaving a resinous mass. This was dissolved in a little hot formic acid of sp. gr. 1.22, and from this solution the dibromo-acid slowly separated as a crystalline crust which, after draining on porous porcelain and washing with formic acid, melted at 149—151°. On analysis:

0.1097 gave 0.1325 AgBr. Br = 51.0.

$\text{C}_7\text{H}_{10}\text{O}_4\text{Br}_2$  requires Br = 50.3 per cent.

*cis*-Dibromodimethylglutaric acid is sparingly soluble in water, but on boiling with water is readily decomposed with elimination of hydrogen bromide.

The alkaline methyl alcoholic mother liquors, from which the potassium salt of the *cis*-acid had separated, as just explained, were mixed with water and boiled until free from methyl alcohol, neutralised, and treated at 0° with a slight excess of permanganate to destroy any trace of the *cis*-acid and other impurities. After removing the excess of permanganate, filtering from the manganese precipitate, and evaporating to dryness, the mass was acidified and the ether extract digested with acetic anhydride. The crude anhydride thus formed yielded, after fractionation and hydrolysis, a small quantity of  $\alpha\alpha$ -dimethylglutaric acid, which melted at 85—87° and was apparently not quite so pure as the specimen of this acid obtained as explained on p. 13.

*Conversion of  $\beta$ -Hydroxy- $\alpha\alpha$ -dimethylglutaric Acid into trans- $\alpha\alpha$ -Dimethylglutaconic Acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ .*

This conversion may be effected either by heating the hydroxy-acid or by treating it with phosphorus pentachloride.

I. The hydroxy-acid, in quantities of about 0.5 gram, was rapidly distilled under a pressure of 60 mm. from a small retort. The acid melted and then effervesced vigorously owing to the escape of water vapour and some carbon dioxide, and a thick oil smelling strongly of a fatty acid distilled over, the distillate becoming semi-solid on cooling. When rubbed with hydrochloric acid, the oily impurity dissolved, leaving a crystalline mass which, in contact with porous porcelain, became hard and colourless and melted at about 135—145°. After extracting with toluene and repeatedly recrystallising the residue from water, the melting point rose to 168—172°. On analysis:



0.1106 gave 0.2152 CO<sub>2</sub> and 0.0642 H<sub>2</sub>O. C = 53.0 ; H = 6.3.

C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> requires C = 53.2 ; H = 6.3 per cent.

That this acid was *trans*-αα-dimethylglutaconic acid was proved by mixing a small quantity with an equal amount of a specimen of this acid which had been prepared by another process (Perkin, *Trans.*, 1902, 81, 253), when no lowering of the melting point could be observed.

From the mother liquors of this acid, a small quantity of an acid melting at 133—135° was isolated, which possibly consisted of the corresponding *cis*-modification, but the quantity was too small for identification. Since αα-dimethylglutaconic acid is slowly decomposed on distillation into vinyl dimethylacetic acid and carbon dioxide (*loc. cit.*, p. 256), it follows that a considerable loss of this acid must have taken place during the above process. Much better results were subsequently obtained in the following way :

II. The hydroxy-acid (2 grams) is heated with phosphorus pentachloride (11 grams), first on the water-bath for half-an-hour and then for 15 minutes to boiling, and the product, after cooling, poured into alcohol. Water is then added, the heavy oil extracted with ether, the ethereal solution washed with sodium carbonate, dried over calcium chloride, and evaporated. The oil, after standing over sulphuric acid in a vacuum desiccator for some hours, gave, on analysis, the following results, which show that it evidently consisted of slightly impure ethyl β-chloro-αα-dimethylglutaconate,



0.2984 gave 0.1526 AgCl. Cl = 12.7.

C<sub>11</sub>H<sub>19</sub>O<sub>4</sub>Cl requires Cl = 14.1 per cent.

The oil was digested with twice its volume of diethylaniline for 10 minutes, poured into dilute hydrochloric acid, extracted with ether, and the ether distilled off. The residue was hydrolysed with methyl alcoholic potash and, after the methyl alcohol had been removed by evaporating with water, acidified and extracted several times with ether. The ethereal solution was carefully dried over calcium chloride and evaporated to a small bulk when, on standing, a colourless acid separated which crystallised from water in leaflets, melted at 172°, and consisted of pure *trans*-αα-dimethylglutaconic acid :

0.1251 gave 0.2442 CO<sub>2</sub> and 0.0725 H<sub>2</sub>O. C = 53.2 ; H = 6.4.

C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> requires C = 53.2 ; H = 6.3 per cent.

The ethereal mother liquors from this acid, on evaporation, deposited a yellow oil which almost completely solidified on standing and, in contact with porous porcelain, yielded a hard mass of crystals. This acid, after twice crystallising from water, melted at 168—172° and

consisted of the *trans*-acid; the total yield of this acid obtained from the hydroxy-acid by the above process was nearly quantitative, there being apparently no trace of the *cis*-acid formed.

*trans*- $\beta\gamma$ -Dibromo- $\alpha\alpha$ -dimethylglutaric Acid,



—*trans*-Dimethylglutaconic acid is much less readily attacked by bromine than the corresponding *cis*-acid since, unlike the latter, it is not converted into its dibromide when left in contact with bromine vapour for 12 hours. When, however, the finely powdered acid was rubbed in a mortar with dry bromine, it dissolved, and after standing for 2 hours and removing the excess of bromine in a current of air, a nearly colourless mass was obtained which crystallised from formic acid of sp. gr. 1.22 in small, glistening needles.

These melted with vigorous decomposition at about 215—217° and consisted of pure *trans*-dibromodimethylglutaric acid. On analysis:

0.2395 gave 0.2847 AgBr. Br = 50.5.

$\text{C}_7\text{H}_{10}\text{Br}_2\text{O}_4$  requires Br = 50.3 per cent.

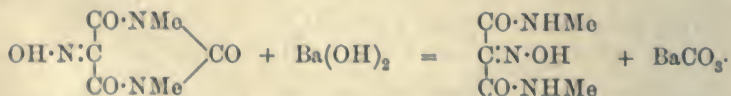
In conclusion, we wish to express our thanks to Mr. D. Trevor Jones, B.Sc., for his valuable assistance in carrying out these experiments.

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### III.—Note on the Action of Barium Hydroxide on Dimethylvioluric Acid.

By MARTHA ANNIE WHITELEY.

ANDREASCH (*Monatsh.*, 1895, 16, 17) was the first to investigate the behaviour of dimethylvioluric acid towards boiling barium hydroxide, and found that the chief products were isonitrosomalondimethylamide and barium carbonate, whilst a little methylamine sulphate was present in the acidified mother liquors. The reaction was therefore represented by the following equation:



This method was employed for the preparation of the isonitrosomalondimethylamide required for the investigation on the isonitroso-derivatives of substituted malonamides. The method was found to

be quite satisfactory, but the properties of the compound were so entirely different from those ascribed to it by Andreasch that the reaction was submitted to a careful investigation. The results show that although isonitrosomalondimethylamide is the chief out of the *seven* products of the reaction, it is doubtful if Andreasch ever isolated it.

Andreasch obtained his dimethylviouric acid from caffeine by a somewhat long and tedious process. In the preparation of the dimethylviouric acid used in this investigation, a saving of time and material was obtained by reverting to the older method of oxidising caffeine by chlorine water (Rochleder, *Annalen*, 1849, 71, 1). Ten grams of caffeine were dissolved in the least possible quantity of boiling water and the caffeine precipitated in the form of a felted mass of crystals by cooling. Chlorine was passed through the semi-solid mass until all had dissolved, and the addition of concentrated aqueous potash to a drop of the solution did not precipitate caffeine. The excess of chlorine was removed by passing a current of air through the liquid; 4.5 grams of hydroxylamine hydrochloride were then added and the mixture gently warmed on a steam-bath for half-an-hour. On rapidly cooling the contents of the flask, the dimethylviouric acid separated in the form of fine needles, which were the pure hydrated form of the acid melting at 127°. The yield amounted to 43 per cent. of the theoretical. Recrystallisation from alcohol or water effected no change in the melting point:

0.1144 gave 21.2 c.c. moist nitrogen at 751 mm. and 20°.  $N = 20.95$ .

$C_6H_7O_4N_3 \cdot H_2O$  requires  $N = 20.70$  per cent.

On drying in the steam oven, the anhydrous acid was obtained; it melted at 141° (Fischer and Ach, *Ber.*, 1895, 28, 3143):

0.6667 lost 0.0599  $H_2O$  on drying at 100°.  $H_2O = 8.95$ .

0.1752 gave 34.3 c.c. moist nitrogen at 755.5 mm. and 18.7°.  $N = 22.38$ .

$C_6H_7O_4N_3$  requires  $N = 22.73$  per cent.

$C_6H_7O_4N_3 \cdot H_2O$  requires  $H_2O = 8.89$  per cent.

The hydrated acid also loses its water when the finely powdered crystals are exposed over sulphuric acid for several hours; the unbroken crystals do not lose in weight when kept in a vacuum over sulphuric acid for 16 hours. The hydrated acid becomes strongly electrified by pressure or friction; this property is not possessed by the dehydrated compound.

The copper salt of dimethylviouric acid is volatile, forming a green vapour closely resembling that of the copper haloid salts.

*Action of Barium Hydroxide on Dimethylviouric Acid.*—Mixed solutions of 10 grams of dimethylviouric acid and 30 grams of crystallised barium hydroxide were boiled until the deep purple colour



changed to a bright yellow; a white precipitate was thrown down and there was a strong odour of methylamine. The mixture was filtered, and the precipitate, which when dry weighed 19 grams, was found to be a mixture of 94 per cent. of barium carbonate and 6 per cent. of barium oxalate. The clear yellow filtrate was treated with dilute sulphuric acid until the yellow colour disappeared, the precipitated barium sulphate removed by filtration, and the colourless filtrate evaporated to a small bulk on the steam-bath. On cooling, a mass of bright, shining, crystalline scales with a pearly lustre separated. These, when collected, washed, and dried, weighed 2 grams (see *A*); the filtrate was placed in a vacuum over sulphuric acid for several days; it formed a slightly moist, crystalline mass weighing 7.4 grams. The viscous mass was separated by filtration into a pale yellow liquid weighing 4 grams (see *B*), and a crystalline solid which, after washing with alcohol and ether and drying, weighed 2.8 grams (see *C*).

(i) *A* proved to be monomethyloxamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_3$ ; it consisted of shining, white scales with a pearly lustre, melted at  $228\text{--}230^\circ$ , and was sparingly soluble in alcohol and boiling water, readily crystallising from the latter. After three recrystallisations, the melting point was constant at  $231\text{--}232^\circ$ . It sublimed readily on heating, the sublimate consisting of a feathery mass of crystals having the same melting point as the original substance. The results of the analyses of various specimens are given:

0.1967 gave 0.2565  $\text{CO}_2$  and 0.1105  $\text{H}_2\text{O}$ .  $\text{C} = 35.57$ ;  $\text{H} = 6.27$ .

0.1873 „ 0.2421  $\text{CO}_2$  „ 0.1051  $\text{H}_2\text{O}$ .  $\text{C} = 35.27$ ;  $\text{H} = 6.28$ .

0.1468 „ 35.5 c.c. moist nitrogen at  $18.5^\circ$  and 745 mm.  $\text{N} = 27.29$ .

0.1110 „ 26.6 c.c. „ „  $17^\circ$  „ 752 mm.  $\text{N} = 27.52$ .

$\text{C}_3\text{H}_6\text{O}_2\text{N}_2$  requires  $\text{C} = 35.28$ ;  $\text{H} = 5.92$ ;  $\text{N} = 27.49$  per cent.

Monomethyloxamide is described by Wallach (*Annalen*, 1876, 184, 70) as crystallising in microscopic needles melting and subliming at  $227\text{--}229^\circ$ :

(ii) *B* consisted of a viscid liquid which gave a white, crystalline precipitate with alcohol. This was identified as methylamino sulphate by its ready solubility in water, its deliquescent nature, the evolution of methylamine when warmed with potash, and the formation of a precipitate of barium sulphate on the addition of barium chloride to the aqueous solution.

The alcoholic filtrate from which the methylamine sulphate had been separated was evaporated to dryness and the crystalline residue added to *C*.

(iii) *C* was a white, crystalline substance, from which, by repeated fractional crystallisation from ethyl acetate, alcohol, and water, three substances were isolated,  $\text{C}_1$ ,  $\text{C}_2$ , and  $\text{C}_3$ .

$C_1$ .—This was proved to be isonitrosomalondimethylamide; it was found in much larger quantity than any of the other products. It is a white, crystalline substance readily soluble in alcohol, ethyl acetate, glacial acetic acid, acetone, or water, crystallising from dilute aqueous solution in well-developed, flattened prisms elongated parallel to the  $b$ -axis.

The pinacoid faces  $a\{100\}$  and  $c\{001\}$ , also the prism face  $q\{011\}$ , are present on all the crystals. In a few crystals there are, in addition, a dome face  $r\{10\bar{1}\}$  and a prism face  $p\{120\}$ . Good reflections are obtained from all the faces except the prism face  $p\{120\}$ , which is usually ridged.

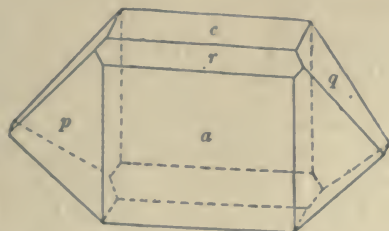
There is a perfect plane of cleavage parallel to  $a\{100\}$ , and thin sections suitable for optical examination are readily obtained.

When a thin section parallel to  $a\{100\}$  is viewed between crossed nicols in parallel light, there is a well-marked extinction parallel to the edge formed by the prism face  $q\{011\}$ . In convergent light, a very clear optic axial figure is seen through the face  $a\{100\}$ . The optic axial plane is perpendicular to the plane of symmetry  $(010)$ , the acute bisectrix being nearly perpendicular to the form  $a\{100\}$ . The double refraction is negative. The dispersion of the optic axes is very slight.

*Crystalline System.*—Monosymmetric.

$$a : b : c = 1.53394 : 1 : 0.88680$$

$$\beta = 68^\circ 43'.$$



| Angle.                 | Number of observations. | Limits.                         | Mean.           | Calculated.     |
|------------------------|-------------------------|---------------------------------|-----------------|-----------------|
| $ac = 100 : 001$       | 22                      | $69^\circ 12' - 68^\circ 18'$   | $68^\circ 43'$  | —               |
| $ac = 100 : 001$       | 12                      | $111^\circ 38' - 110^\circ 55'$ | $111^\circ 20'$ | $111^\circ 17'$ |
| $aq = 100 : 011$       | 14                      | $106^\circ 49' - 106^\circ 4'$  | $106^\circ 19'$ | $106^\circ 15'$ |
| $aq = 100 : 011$       | 13                      | $73^\circ 58' - 73^\circ 18'$   | $73^\circ 40'$  | $73^\circ 45'$  |
| $aq = 001 : 011$       | 35                      | $40^\circ 5' - 39^\circ 9'$     | $39^\circ 34'$  | —               |
| $qq = 011 : 01\bar{1}$ | 17                      | $101^\circ 30' - 100^\circ 30'$ | $100^\circ 51'$ | $100^\circ 52'$ |
| $qp = 100 : 120$       | 9                       | $71^\circ 5' - 70^\circ 23'$    | $70^\circ 41'$  | $70^\circ 43'$  |
| $pp = 120 : 120$       | 4                       | $39^\circ 12' - 38^\circ 14'$   | $38^\circ 43'$  | $38^\circ 34'$  |
| $ar = 100 : 10\bar{1}$ | 9                       | $77^\circ 16' - 76^\circ 36'$   | $77^\circ 0'$   | —               |
| $cr = 101 : 101$       | 8                       | $34^\circ 55' - 33^\circ 44'$   | $34^\circ 15'$  | $34^\circ 17'$  |

My thanks are due to Prof. Armstrong for the opportunity of measuring these crystals in the Crystallography Laboratory of the Central Technical College.

*iso*Nitrosomalondimethylamide melts at  $157^{\circ}$ ; it evolves methylamine on warming with aqueous potash, and is therefore a methylamide, also it readily splits off hydroxylamine on warming with hydrochloric acid, and is therefore an oxime. It dissolves in alkalis with a bright yellow colour, the colour changing to violet on the addition of ferrous sulphate; from the coloured solution, after a few minutes, shining, bronze-coloured crystals are deposited:

0.1129 gave 26 c.c. moist nitrogen at  $19^{\circ}$  and 758 mm.  $N = 26.40$ .

0.1004 „ 23.5 c.c. „ „  $20^{\circ}$  „ 751 mm.  $N = 26.47$ .

$C_5H_9O_3N_3$  requires  $N = 26.45$  per cent.

The *potassium* salt,  $(CO \cdot NHMe)_2C:N \cdot OK$ , is a bright yellow, crystalline solid, readily soluble in water, but less so in alcohol. It was recrystallised from moist alcohol:

0.2338 gave 0.1031  $K_2SO_4$ .  $K = 19.78$ .

$C_5H_8O_3N_3K$  requires  $K = 19.81$  per cent.

The *ferrous* salt,  $[(CO \cdot NHMe)_2C:N \cdot O]_2Fe$ , was precipitated in the form of purple crystals with a bronze lustre by adding ferrous sulphate solution to a slightly alkaline solution of the oxime. The dry salt is insoluble in water:

0.1390 gave 0.02953  $Fe_2O_3$ .  $Fe = 14.87$ .

$(C_5H_8O_3N_3)_2Fe$  requires  $Fe = 15.04$  per cent.

$C_2$ .—This consisted of shining, white, leafy crystals with a pearly lustre, readily soluble in cold water and insoluble in alcohol; it was recrystallised by adding alcohol to a concentrated aqueous solution. The melting points of various specimens varied from  $170$ — $178^{\circ}$  with slight decomposition. The aqueous solution gave no colour reaction with ferrous sulphate and an alkali. On warming with aqueous potash, it evolved methylamine, and on boiling with hydrochloric acid hydroxylamine was not produced. It is probably *methylamine oxamate*,  $NH_2 \cdot CO \cdot CO_2 \cdot NH_3Me$ :

0.1380 gave 28.1 c.c. moist nitrogen at  $19.75^{\circ}$  and 767 mm.  $N = 23.54$ .

0.1386 „ 27.6 c.c. „ „  $16.25^{\circ}$  „ 771.5 mm.  $N = 23.56$ .

$C_3H_8O_3N_2$  requires  $N = 23.37$  per cent.

$C_3$ .—This substance resembled  $C_2$  in solubility; it crystallised in beautiful, long needles from hot water and alcohol. After repeated crystallisation, the melting point was constant at  $239$ — $240^{\circ}$  with decomposition. The solution gave no coloration with ferrous sulphate



and an alkali. It evolved methylamine on warming with aqueous potash. It did not evolve hydroxylamine on boiling with hydrochloric acid :

0.1863 gave 0.1570  $\text{CO}_2$  and 0.1053  $\text{H}_2\text{O}$ . C = 23.00 ; H = 6.32.

0.2229 „ 0.1863  $\text{CO}_2$  „ 0.1200  $\text{H}_2\text{O}$ . C = 22.81 ; H = 6.02.

0.1317 „ 29.8 c.c. moist nitrogen at  $19^\circ$  and 766 mm. N = 26.09.

The substance does not contain water of crystallisation, for it did not lose in weight on drying at  $100^\circ$ . When heated at  $120^\circ$ , it probably sublimed a little, as there was a small but fairly constant loss in weight.

The results of analyses point to the empirical formula  $\text{C}_4\text{H}_{13}\text{O}_6\text{N}_4$ , which requires C = 22.52 ; H = 6.14 ; N = 26.23 per cent., but owing to the small quantity of material the substance has not been identified.

The decomposition of dimethylviouric acid by barium hydroxide is therefore a somewhat complicated reaction ; among the products, the following substances have been identified : *iso*Nitrosodimalonmethylamide ; carbon dioxide and oxalic acid (as barium salts) ; monomethyloxamide ; methylamine ; methylamine oxamate. Andreasch obtained only carbon dioxide, methylamine, and a crystalline compound melting at  $228^\circ$ , which, on analysis, gave numbers corresponding with those required for *isonitrosomalondimethylamide*.

It was at first thought that this might be an isomeric form of *iso*-nitrosomalondimethylamide which has been shown above to have quite different properties, but though the experiment has been repeated several times with every precaution, no isomeride has been isolated from the mixture. Andreasch's compound corresponds closely in appearance, solubility, and melting point with monomethyloxamide, the only solid which has been found to separate from the filtrate on evaporation, and it is not improbable that he analysed an impure specimen of monomethyloxamide (the melting point of his compound being  $3^\circ$  lower than that of pure monomethyloxamide). This is the more probable as the percentage of nitrogen in his compound, from the data given,\* is 25.36, and not 26.60 as stated. This is assuming the nitrogen to be moist, a conclusion justified by reference to other analyses quoted in the paper.

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\* 0.1525 gave 34.6 c.c. nitrogen at  $21^\circ$  and 746.5 mm.

# IV.—The Oxime of Mesoxamide and some Allied Compounds. Part II. Disubstituted Derivatives.

By MARTHA ANNIE WHITELEY.

THE investigation which forms the subject of this paper is a continuation of the work on the oximes of mesoxamide and its dimethyl derivative (Whiteley, Trans., 1900, 77, 1040): compounds characterised by their bright yellow alkali and rich violet ferrous salts. From the constitution of the original compound, it is clear that the acidic hydrogen is furnished either by one of the  $-\text{CO}\cdot\text{NH}_2$  groups reacting in the tautomeric form  $-\text{C}(\text{OH})\text{:NH}$ , or by the oximino-group itself.

The possibility of the acidic hydrogen being derived from one of the  $-\text{CO}\cdot\text{NH}_2$  groups was first of all examined, as this explanation had suggested itself at the time the previous communication was published (*loc. cit.*, p. 1045). A series of compounds was therefore prepared in which alkyl or aryl radicles replace partially or wholly the hydrogen atoms of the original amido-groups.

A list of the compounds examined, their colours, and the colours of the alkali and ferrous salts obtained from them is given in the following table :

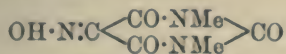
|   | Colour of   |              |               |
|---|---|--------------|---------------|
|   | Oxime.  | Alkali salt. | Ferrous salt. |
| $(\text{CO}\cdot\text{NH}_2)_2\text{C}\text{:N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalonomamide.   | $\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$ | Yellow       | Violet.*      |
| $(\text{CO}\cdot\text{NHMe})_2\text{C}\text{:N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalondimethylamide.   | Colourless  | Yellow       | Violet        |
| $(\text{CO}\cdot\text{NHPh})_2\text{C}\text{:N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalonanilide.   | $\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$ | Yellow       | Blue          |
| $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}\cdot\text{NH}_2)_2\text{N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalonumono- <i>p</i> -tolylamide. | Yellow  | Yellow       | Purple        |
| $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\text{:N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalondi- <i>p</i> -tolylamide.                                 | $\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$ | Yellow       | Blue          |
| $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\text{:N}\cdot\text{OH}$<br><i>iso</i> Nitrosomalondi- <i>o</i> -tolylamide.                                 | $\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$ | Yellow       | Blue          |
| $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})_2\text{N}\cdot\text{OH}$<br>Ethyl <i>iso</i> nitrosomalon- <i>o</i> -tolylamate.     | Yellow  | Yellow       | Purple        |

\* Ferrous potassium salt.

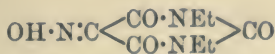


|  | Colour of   |   |  |
|--|---|---|--|
|  | Oxime.  | Alkali salt.  | Ferrous salt.  |
| $(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$<br><i>α</i> -Nitrosomalondi- <i>α</i> -naphthylamide. | Orange  | Yellow  | Blue   |
| $(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$<br><i>α</i> -Nitrosomalondi- <i>β</i> -naphthylamide. | Yellow  | Yellow  | Blue   |
| $(\text{CO}\cdot\text{NMePh})_2\text{C}\cdot\text{N}\cdot\text{OH}$<br><i>α</i> -Nitrosomalondimethylanilide.                                      | $\begin{cases} \alpha & \text{Colourless} \\ \beta & \text{Yellow} \end{cases}$ | $\begin{cases} \alpha & \text{Yellow} \\ \beta & \text{Colourless} \end{cases}$ | $\begin{cases} \alpha & \text{Purple} \\ \beta & \text{—}^*$ |

From these results, it follows that the replacement of one or both aminic hydrogen atoms of the  $-\text{CO}\cdot\text{NH}_2$  groups does not interfere in any way with the production of yellow alkali salts and violet or blue ferrous salts. The acidic hydrogen, therefore, of the oxime of mesoxamide and its derivatives is *not* furnished by either of the  $-\text{CO}\cdot\text{NH}_2$  groups. Further evidence in favour of this view is afforded by the alkyl-substituted violuric acids, monomethylvioluric acid (Andreasch, *Monatsh.*, 1900, 21, 281), dimethylvioluric acid (Andreasch, *Monatsh.*, 1895, 16, 17), and diethylvioluric acid (Sembritzki, *Ber.*, 1898, 30, 1814), all of which give the red alkali salts and deep blue ferrous salts characteristic of the group, whilst neither of the last two compounds contains a  $-\text{CO}\cdot\text{NH}-$ , complex as the formulæ show



Dimethylvioluric acid.



Diethylvioluric acid.

Dismissing, therefore, the view that the  $-\text{CO}\cdot\text{NH}_2$  group furnishes the acidic hydrogen, attention was then concentrated on the oximino-group, and a number of substances were examined with the object of ascertaining the conditions under which compounds containing this group yield coloured salts. The formation of yellow alkali salts is characteristic of *α*-oximinoketones, to which class the oximes under discussion belong. Schramm (*Ber.*, 1883, 16, 183) first drew attention to this influence of a neighbouring radicle on the acid character of the oximino-group, and, later, Guinchard (*Ber.*, 1900, 32, 1723) pointed out the difference in colour of the alkali salts of this class according as they are open chain or ring compounds, the former yielding yellow, the latter red to violet salts. The purple or blue ferrous salts are, however, much more strikingly characteristic of the oximes under discussion than the yellow alkali salts, and yet with the exception of violuric acid and its mono- and di-substituted alkyl derivatives no reference to the production of coloured ferrous salts by oximes of this class

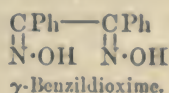
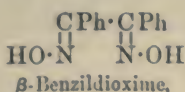
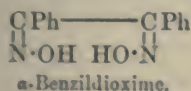
\* No ferrous salt. Crimson ferric salt.

has been met with in the literature. In view of this seeming omission, a number of  $\alpha$ -oximinoketones were prepared and examined with respect to their behaviour with ferrous sulphate and an alkali; the results are recorded in the following table:

|  | Colour of    |                 |
|--|--------------|-----------------|
|  | Alkali salt. | Ferrous salt.   |
| $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$<br><i>iso</i> Nitrosoacetone.   | Yellow       | Blue            |
| $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO}_2 \text{Et}$<br>Ethyl <i>isonitroso</i> acetoacetate.                                      | Yellow       | Blue            |
| $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO}_2 \text{Et}$<br>Ethyl <i>isonitroso</i> benzoylacetate.                           | Yellow       | Blue            |
| $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{CH}_3$<br><i>iso</i> Nitrosoacetylacetone.                                     | Yellow       | Blue            |
| $\text{C}_2\text{H}_5 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{CH}_3$<br>$\gamma$ - <i>iso</i> Nitroso- $\beta$ -ketopentane.                        | Yellow       | Blue            |
| $\text{CH}_3 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{NH}_2$<br>Oxime of pyruvamide.   | Yellow       | Reddish-brown   |
| $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{CO} \\   \\ \text{C} \cdot \text{N} \cdot \text{OH} \end{array}$<br><i>iso</i> Nitrosocamphor.                           | Yellow       | Blue            |
| $\text{Ph} \cdot \text{C} \cdot \text{CO} \cdot \text{Ph}$<br>$\text{N} \cdot \text{OH}$<br>$\parallel$<br>$\alpha$ -Benzilmonoxime.   | Yellow       | Blue            |
| $\text{Ph} \cdot \text{C} \cdot \text{CO} \cdot \text{Ph}$<br>$\text{HO} \cdot \text{N}$<br>$\parallel$<br>$\beta$ -Benzilmonoxime.  | Yellow       | No ferrous salt |
| $\text{N} \begin{array}{c} \diagup \text{CPh} \\ \diagdown \text{O} \cdot \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$<br><i>iso</i> Nitrosophenylisoxazolone. | Red          | Greenish-blue   |
| $\text{N} \begin{array}{c} \diagup \text{CMe} \\ \diagdown \text{O} \cdot \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$<br><i>iso</i> Nitrosomethylisoxazolone. | Red          | Chocolate-brown |

Of the compounds tabulated, two only, the monoximes of benzil, exhibit isomerism, and one of these affords the only exception to the formation of a ferrous salt of characteristic colour by the  $\alpha$ -oximinoketones which have been examined. Attention was therefore directed to the stereoisomeric oximes, and the dioximes of benzil, the series most readily prepared, were investigated, with the result that, whilst these compounds gave a pale yellow colour with alkalis, they showed a

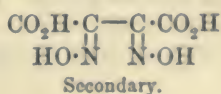
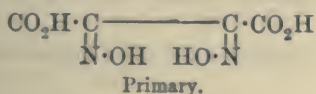
difference of behaviour on the further addition of ferrous sulphate;  $\alpha$ -benzildioxime gave a rich, purple colour;  $\beta$ -benzildioxime gave no trace of a coloration, and  $\gamma$ -benzildioxime gave a reddish-purple colour changing rapidly to the dark brown of ferric hydroxide. Representing these substances by the constitutional formulæ assigned to them by Beckmann and Köster (*Annalen*, 1893, 274, 32), it will be seen that the *syn*-isomeride forms a stable purple ferrous salt, the *amphi*-isomeride an unstable purple ferrous salt, whilst the *anti*-isomeride is destitute of colour-giving properties:



These compounds present a further point of interest in that they are diketoximes, and the fact of all three yielding yellow alkali salts, and one of them a purple ferrous salt, indicates that the radicle  $\text{=C:N} \cdot \text{OH}$ , like carbonyl itself, can sometimes influence the acidic nature of a contiguous oximino-group. This conclusion is opposed to that drawn by Schramm (*Ber.*, 1883, 16, 183), who attributed the non-formation of coloured alkali salts from methylglyoxime to the inoperative character of two oximino-groups as compared with the colour-giving property of the carbonyl-oximino-group in *isonitrosoacetone* (methylglyoxaldoxime).

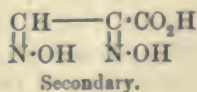
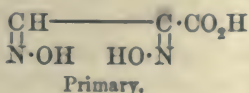
In the literature of the dioximes, only two cases could be found in which mention is made of the production of a coloured ferrous salt by compounds of this class; these are the two dioximes of dihydroxy-tartaric acid (Söderbaum, *Ber.*, 1892, 24, 1215) and the two dioximinopropionic acids (Söderbaum, *Ber.*, 1893, 25, 905). The formulæ ascribed to them are as follows:

*Dioximes of dihydroxytartaric acid.*



Violet-red coloration with ferrous sulphate and an alkali.

*Dioximinopropionic acids.*



Fleeting dark violet coloration with ferrous sulphate and caustic alkali.

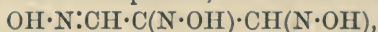


The fact that each of the isomeric forms of these two compounds gives the colour reaction is not surprising, since in addition to being a dioxime each contains the grouping  $\begin{array}{c} -\text{CO}\cdot\text{C}- \\ | \\ \text{HO}\cdot\text{N} \end{array}$ , which is present in  $\alpha$ -benzilmonoxime.

In each case, Söderbaum succeeded in obtaining two isomeric forms of his dioximes out of the three and four theoretically possible; this is of especial interest, because isomerism in oximes of the aliphatic series is of rare occurrence. A few dioximes of this series in which no isomeric forms could be obtained were prepared, and each was found to give a characteristic coloration with ferrous sulphate and an alkali:

|  | Colour of    |               |
|--|--------------|---------------|
|  | Alkali salt. | Ferrous salt. |
| $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{Et}$<br>Oxime of ethyl isonitrosoacetoacetate. | Colourless   | Violet        |
| $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_2\text{H}_5$<br>Methylethylglyoxime.                   | Yellow       | Dark brown    |
| $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}$<br>Methylhydroxyglyoxime.                            | Yellow       | Reddish-brown |

Among the trioximino-compounds, oximinomesoxaldoxime,



is described by Pechmann and Wehsarg (*Ber.*, 1889, 21, 2989) as giving a wine-red colour with ferrous sulphate and a violet precipitate on the addition of aqueous soda to the solution.

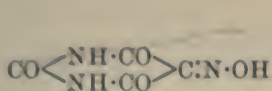
A consideration of the facts so far presented makes it clear that the production of coloured alkali salts by  $\alpha$ -oximinoketones, and, probably, by dioximes, and the production of coloured ferrous salts by these compounds are two distinct phenomena, the former being a general characteristic, whilst the latter is influenced by the isomerism of the oximino-group. These two phenomena must therefore receive separate consideration.

The question of the production of coloured alkali salts by colourless

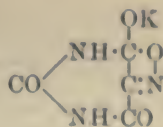
compounds containing the  $\begin{array}{c} | \\ \text{CO} \\ | \\ \text{C}:\text{N}\cdot\text{OH} \\ | \end{array}$  complex has received much

attention from Hantzsch and his pupils (*Ber.*, 1899, 32, 593; Hantzsch and Farmer, *ibid.*, 3101; Guinchard, *ibid.*, 1723). According to Hantzsch, the salts of all  $\alpha$ -oximinoketones have a constitution different from that of the original or pseudo-acid, and they are formed from the latter by an alteration in the relative position of the atoms during the dissociation into ions. Thus in the case of violuric acid:



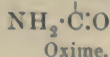
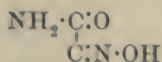


Pseudo-acid.

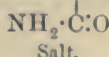
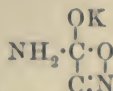


Salt.

In the previous communication (*loc. cit.*, p. 1044), it was pointed out that the formation of coloured salts by the colourless oxime of mesoxamide might be explained by assuming a similar tautomeric change to take place, that is to say, the colourless oxime and its yellow alkali salt may be differently constituted thus :



Oxime.



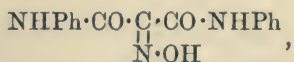
Salt.

The present investigation, however, shows that another interpretation can be given in which no such far-reaching structural modification is involved. If reference be made to page 24, it will be seen that the oxime of mesoxamide itself, and three out of the eight mono- and di-substituted derivatives of it, exist in two forms, one colourless and the other having the yellow colour of the alkali salt. Of the remaining five, one has so far been obtained only in the colourless form, and the other four are yellow.

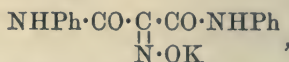
The isomerism observed in this series of compounds is similar to the "tautomerism" discovered by Wislicenus (*Annalen*, 1896, 291, 147) in  $\alpha$ - and  $\beta$ -ethyl phenylformylacetate, and to the "dynamic isomerism" observed by Lowry (*Trans.*, 1899, 75, 211) in nitrocamphor and  $\pi$ -bromonitrocamphor, in so far as the two forms are mutually convertible (1) by the action of solvents, (2) by fusion, and (3) by the action of acids on solutions of the alkali salts. Thus in the case of *isonitrosomalonanilide*, in which the isomerism is most clearly defined, the white isomeride crystallises in brilliant scales with a pearly lustre from a solution of ethyl or methyl alcohol, ethyl acetate, acetone, ether, or acetic acid, whilst from a solution in benzene or chloroform the other isomeride is obtained in the form of bright yellow, prismatic crystals. The white isomeride melts at  $141^\circ$ , the yellow has no apparent melting point, but softens and turns white at  $120$ – $122^\circ$ , and melts at  $141^\circ$ . There is a third form melting at  $124^\circ$ , which appears to be the equilibrium mixture of the other two (compare Lowry, *loc. cit.*, p. 224): it is obtained in tufts of needles of a pale yellow colour by the rapid cooling of hot concentrated solutions of the yellow or white isomeride in any solvent (except methyl or ethyl alcohol), or by rapidly cooling the yellow liquid obtained by the fusion of the white variety. By long

contact with the solvent, this form is converted into the white or yellow isomeride according to the nature of the solvent.

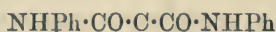
This tautomerism, which occurs in some of the oximes under discussion, has an important bearing on the question of the colour of the alkali salts, for it is not unreasonable to suppose that the difference in structure between the colourless and yellow forms of these oximes is the same as that which obtains between the colourless oximes and their yellow alkali salts. According to Hantzsch's hypothesis, this difference is due to a structural change in which, not only the oximino-, but also the neighbouring carbonyl groups take part; a far simpler explanation, however, is afforded if it is assumed that the structural change affects the oximino-group alone, the colourless isomeride having the *isooximino*-structure, and the coloured form and the alkali salts that of the true oxime (compare Dunstan and Goulding, *Trans.*, 1901, 79, 628) thus:



Yellow *isonitrosomalonanilide*.



Potassium *isonitrosomalonanilide*.



White *isonitrosomalonanilide*.

[ This explanation of the difference in structure between the coloured and colourless isomerides receives considerable support from the fact that the constitution suggested for the former contains the complex  $-\underset{\text{||}}{\text{C}}-\underset{\text{||}}{\text{C}}-\underset{\text{||}}{\text{C}}-$ , which is present in the coloured triketones and their coloured derivatives, and thus belongs to that group which Armstrong, in his classification of coloured organic compounds, calls "pseudo-quinonoid" (*Encyclopædia Britannica*, vol. 26, *Art. Chemistry*, p. 746).

The complex  $-\underset{\text{||}}{\text{C}}-\underset{\text{||}}{\text{C}}-\underset{\text{||}}{\text{C}}-$ , on the other hand, which occurs in the colourless oxime is characteristic of the colourless derivatives of triketones, such as diphenyltriketone (Pechmann and de Naufville, *Ber.*, 1890, 23, 3379), triketopentane (Sachs and Barschall, *Ber.*, 1901, 34, 3047), and phenyltriketobutane (Sachs and Röhmer, *Ber.*, 1902, 35, 3307).

Finally, this explanation of the formation of coloured alkali salts by  $\alpha$ -oximinoketones can be extended to the cases of the yellow alkali salts of nitrosoguanidine and nitrosocarbamide (p. 31), to which Hantzsch's hypothesis cannot be applied.

Passing now to a consideration of the formation of ferrous salts of characteristic colour by  $\alpha$ -oximinoketones and dioximes, no satisfactory explanation of this colour reaction presents itself. With the exception of the soluble ferrous potassium salt of the oxime of mesoxamide, the

coloured compounds are insoluble simple ferrous salts, and do not in any respect, save that of colour, correspond with that curious complex iron compound of carboxime or fulminic acid discovered by Nef (*Annalen*, 1894, 280, 335), which appears to be a salt bearing the same relation to fulminic acid that Prussian blue does to hydrogen cyanide.

Among the fairly large and representative number of  $\alpha$ -oximino-ketones which have been examined in respect of their behaviour with ferrous sulphate and an alkali, one only,  $\beta$ -benzilmonoxime, has failed to give the colour reaction, whilst among the oximes, isomerism again seems to play an important part in this connection. The extension of the investigation to a large number of isomeric mono- and di-oximes may possibly throw some light on this subject, and show how far ferrous sulphate and an alkali is a reagent capable of discriminating between the isomerides.

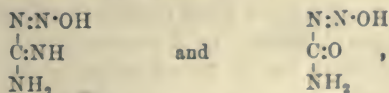
In conclusion, reference must be made to a few compounds not belonging to the oximinoketones or to the dioximes, which give a purple or blue coloration with ferrous sulphate and an alkali. These include alloxan and its mono- and di-alkyl derivatives, which give a blue colour with the reagents. Ethylnitrolic acid, which forms red alkali salts (Meyer and Constam, *Annalen*, 1882, 214, 329), was found to give a characteristic chocolate-brown coloration on the addition of ferrous sulphate to the alkaline solution. Nitrosoguanidine and nitrosocarbamide\* each give a yellow alkali salt and a purple-red colour with ferrous sulphate and an alkali (Thiele, *Annalen*, 1893, 273, 133 ; 1895, 288, 303).

## EXPERIMENTAL.

### I. *Yellow Variety of the Oxime of Mesoxamide.*

In the original preparation of the oxime of mesoxamide (Trans., 1900, 77, 1040), gaseous nitrosyl chloride was passed into

\* From the constitution ascribed to these compounds by Thiele, the acidic hydrogen is iminic, and the salts of a totally different constitution from those of the large class of oximes considered in this paper, with which they are so closely allied in colour. If, however, the salts of these compounds were derived from tautomeric forms of the original substances,



in which the grouping  $\text{:N}\cdot\text{OH}$  is present, they would come into line with those described in this paper, and it is worthy of note in this connection that Hantzsch (*Ber.*, 1899, 32, 592) classes nitrosourethane with the *antidiazohydroxides*,  $\text{R}_1\text{N:N}\cdot\text{OH}$ , because of its acidic nature.



finely powered malonamide suspended in chloroform or ether; the yield of the oxime was so poor, owing to the fact that neither the malonamide nor the oxime was appreciably soluble in the medium, that the use of nitrosyl chloride was abandoned in favour of the nitrous gases evolved by the action of nitric acid (sp. gr. 1.3) on arsenious oxide, which, acting on malonamide in concentrated aqueous solution, gave the oxime, the yield being 40 per cent. of the theoretical.

Later work on the substituted malonamides having shown that a quantitative yield of the oxime could be readily obtained by the action of nitrosyl chloride in a medium in which either the amide or the oxime, or both, were soluble, the action of nitrosyl chloride on malonamide in various organic solvents was examined. In acetic acid, ethyl acetate, methyl alcohol, or ethyl alcohol, in which the amide is sparingly, and the oxime readily, soluble, the reaction proceeded far more readily than had been observed in the case when chloroform was the medium employed. A remarkable difference, however, was observed in the products obtained under these new conditions, for whereas the oxime obtained from the ethyl acetate and methyl alcoholic solutions was colourless and coincided in properties with that previously obtained, the product of the action of nitrosyl chloride on malonamide in alcoholic solution, although agreeing in chemical properties with the original oxime, differed from it in possessing a *bright yellow colour*.

The yellow isomeride is readily soluble in water, forming a yellow solution, which gives, with potash and ferrous sulphate, the rich violet coloration characteristic of the oxime of mesoxamide. It is sparingly soluble in alcohol or ethyl acetate, more readily so in acetone or glacial acetic acid, and crystallises from each solvent in bright yellow, prismatic crystals. After recrystallising once from absolute alcohol and twice from slightly moist alcohol, it was obtained in bright yellow, prismatic crystals, melting with decomposition at 187—188°:

0.1162 gave 31.95 c.c. moist nitrogen at 17° and 763 mm.  $N = 32.06$ .

$C_3H_5O_3N_3$  requires  $N = 32.11$  per cent.

The two forms of the oxime appear to yield identical salts, and from the potassium salt of the yellow variety the colourless oxime is formed by the action of dilute acids.

The *ethyl ether* was prepared from the silver salt of the yellow form by the action of ethyl iodide; it is identical with the corresponding derivatives of the white oxime, is colourless, melts at 150°, and does not depress the melting point of the original ether.

The *silver salt*,  $(CO \cdot NH_2)_2C:N \cdot OAg, 2NH_3$ , is precipitated by the addition of silver nitrate to an aqueous solution of the yellow or white variety of the oxime containing a little ammonia; the precipitate



dissolves readily in excess of ammonia, and from the solution by slow evaporation the salt is obtained in well formed, deep yellow, prismatic crystals, containing two mols. of ammonia, which it loses partially in a desiccator over sulphuric acid, and completely when heated at  $100^{\circ}$ :

I. 0.4529, dried in air, gave 0.1800 Ag. Ag = 39.76 per cent.

$C_5H_4O_3N_3Ag, 2NH_3$  requires Ag = 39.65 per cent.

II. Specimen kept in desiccator for three days:

0.5004 lost 0.0587 at  $100^{\circ}$ , and gave 0.2002 Ag.  $NH_3$  = 11.72; Ag = 45.32.

$C_5H_4O_3N_3Ag, 2NH_3$  requires  $NH_3$  = 12.55 per cent.

$C_5H_4O_3N_3Ag$  requires Ag = 45.32 per cent.

## II. *Malondimethylamide.*

Malondimethylamide was prepared by Freund's method (*Ber.*, 1884, 17, 134) from ethyl malonate and a solution of methylamine ( $33\frac{1}{2}$  per cent.). On mixing the two liquids, there was a development of heat and the ethyl malonate readily passed into solution. The mixture was shaken for six hours and then evaporated on the water-bath to a small bulk; on cooling, malondimethylamide crystallised out, and from the mother liquor by further evaporation a second crop of crystals was obtained. The product was pure (m. p.  $135^{\circ}$ ; Freund gives  $128^{\circ}$ ), and the yield 78 per cent. of the theoretical. Malondimethylamide is very readily soluble in acetone, acetic acid, ethyl or methyl alcohol, or chloroform, but less so in ethyl acetate, sparingly so in benzene, and insoluble in carbon tetrachloride, ether, or light petroleum; it can be most readily crystallised from ethyl acetate or acetone.

*iso*-Nitrosomalondimethylamide,  $(CO \cdot NH \cdot CH_3)_2C : N \cdot OH$ .—Malondimethylamide in solution is very readily converted into the *isonitroso*-derivative by the action of gaseous nitrosyl chloride at  $0^{\circ}$ . Chloroform is the most convenient solvent in which to effect the reaction; the product is pure *isonitrosomalondimethylamide* melting at  $157^{\circ}$ , and the yield is theoretical.

The *isonitrosomalondimethylamide* thus prepared is identical with the compound obtained by the decomposition of dimethylvioluric acid with barium hydroxide; it crystallises in the characteristic monosymmetric prisms, and gives the yellow alkali and the purple ferrous salt (see this vol., page 22).

III. *Malonanilide*.

Malonanilide was prepared by Freund (*Ber.*, 1884, 17, 134) by the condensation of aniline and ethyl malonate. By a slight modification of the method, a yield of 81 per cent. of the theoretical was obtained and the product was pure (m. p. 225°; Freund gives 223°). The aniline and ethyl malonate were heated to gentle boiling in a reflux apparatus for 5 hours; on cooling, a large quantity of malonanilide separated in long, silky needles; these were collected, the mother liquor and alcohol washings concentrated to remove the alcohol, and boiled until, on cooling, the contents of the flask became solid; the solid cake was then broken up, ground with alcohol, filtered, washed, dried, and used in the preparation of the *isonitroso*-derivative.

*isoNitrosomalonanilide*,  $(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2\text{C}\cdot\text{N}\cdot\text{OH}$ .—All attempts to prepare *isonitrosomalonanilide* by the action of nitrous acid on malonanilide were fruitless. Owing to its insolubility in water, acids, or alkali, malonanilide is not acted on by potassium nitrite and sulphuric acid, and it is unchanged when suspended in water and submitted to the action of a stream of nitrous gases from arsenious oxide and nitric acid. When sealed in a tube with the liquefied gases, no *isonitroso*-compound could be separated from the mixture. Amyl nitrite or ethyl nitrite has no action on the compound.

*isoNitrosomalonanilide* was, however, readily prepared from malonanilide by the action of nitrosyl chloride. The malonanilide was suspended in chloroform, in which it is insoluble, and a stream of nitrosyl chloride passed through the mixture until all the solid had passed into solution and the liquid was saturated at 0° with the gas. By spontaneous evaporation, *isonitrosomalonanilide* was obtained as a yellow, crystalline solid melting at 124°; the product was pure and the yield quantitative. The substance is very readily soluble in benzene, chloroform, acetone, ethyl acetate, or methyl alcohol, but less so in alcohol, acetic acid, or carbon tetrachloride, and dissolves only sparingly in ether, light petroleum, or water. It crystallises from a hot concentrated alcoholic solution in the form of pure white, crystalline scales with a pearly lustre; chloroform solutions on complete evaporation deposit bright yellow, prismatic needles; from a concentrated benzene solution, pale yellow needles separate, which, when left in contact with the solvent for several days, slowly change into well formed, thick, flat prisms of a bright yellow colour. From ethyl acetate, methyl alcohol, ether, or acetic acid, on slow evaporation, the white, pearly scales are deposited, and the crust on the walls of the vessel is a mixture of yellow and white crystalline matter.

*Effect of Fusion*.—When the white isomeride of *isonitrosomalon*-

anilide is heated in a capillary tube, it softens and becomes yellow at  $138-140^{\circ}$ , and melts to a yellow liquid at  $141^{\circ}$ ; on cooling gradually, the yellow liquid solidifies to a mixture of white and yellow crystalline matter. When the mixture is reheated, the yellow portion melts at  $124^{\circ}$  and the white remains floating in the yellow liquid until the temperature reaches  $141^{\circ}$ , when it also melts. If the yellow liquid formed by the melting of the white isomeride at  $141^{\circ}$  is rapidly cooled, the solid product appears to be uniformly yellow, and on rapidly heating melts completely at  $124^{\circ}$ . The flat, yellow prisms formed by the prolonged action of benzene on the yellow needles also become white at  $120-122^{\circ}$  and melt at  $141^{\circ}$ .

It is evident from these facts that isonitrosomalonanilide exists in tautomeric forms, one yellow and one white, differing in solubility and melting point. The yellow needles melting at  $124^{\circ}$  appear to be the equilibrium mixture of the two isomerides.

The specimen used for analysis was white and melted at  $141^{\circ}$ :

0.2324 gave 30.8 c.c. moist nitrogen at  $24^{\circ}$  and 766 mm.  $N = 14.98$ .

$C_{15}H_{13}O_3N_3$  requires  $N = 14.86$  per cent.

The *potassium* salt,  $(CO \cdot NH \cdot C_6H_5)_2C : N \cdot OK$ , crystallises in long, thin, silky needles of a bright yellow colour, and is readily soluble in hot alcohol or water:

0.2434, dried at  $100^{\circ}$ , gave 0.0650  $K_2SO_4$ .  $K = 11.98$ .

$C_{15}H_{12}O_3N_3K$  requires  $K = 12.17$  per cent.

*Regeneration of the isoNitroso-derivative from the Potassium Salt.*—

Carbon dioxide was passed through an aqueous solution of the potassium salt until no further precipitate was produced. The precipitate, which was white in colour, was filtered off, washed, and dried; it melted at  $140^{\circ}$  to a yellow liquid, which solidified to a yellow solid and then melted at  $124^{\circ}$ . Sulphuric acid or acetic acid also precipitated the white isomeride from solutions of the alkali salt.

The *ferrous* salt,  $[(CO \cdot NH \cdot C_6H_5)_2C : NO]_2Fe$ , was precipitated in the form of a dark blue solid, not unlike Prussian blue, when ferrous sulphate solution was added to an aqueous solution of the potassium salt; it was not possible to recrystallise it owing to its insoluble nature, so for the purpose of analysis it was well washed, dried in a vacuum over sulphuric acid, and finally at  $100^{\circ}$ :

0.2404 gave 0.0319  $Fe_2O_3$ .  $Fe = 9.29$ .

$C_{20}H_{24}O_6N_6Fe$  requires  $Fe = 9.03$  per cent.

*Acid Silver Salt*,  $(CO \cdot NH \cdot C_6H_5)_2C : N \cdot OAg, (CO \cdot NH \cdot C_6H_5)_2C : N \cdot OH$ .—By the action of aqueous silver nitrate on an alcoholic solution of isonitrosomalonanilide, a yellow silver salt was obtained as a flocculent



precipitate. Before analysis, it was extracted two or three times with boiling alcohol to remove traces of unchanged *isonitrosomalonalanilide*:

0.2559 gave 0.0413 Ag.  $\text{Ag} = 16.15$ .

$\text{C}_{30}\text{H}_{25}\text{O}_6\text{N}_6\text{Ag}$  requires  $\text{Ag} = 16.03$  per cent.

#### IV. *Malondi-p-tolylamide*, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$ .

This compound was prepared by Guthzeit and Laska (*J. pr. Chem.*, 1898, [ii], 58, 414) by the action of *p*-toluidine on the triethyl ester of isaconitic acid,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , and is described as crystallising well from alcohol in silky needles and melting at  $248^\circ$ .

For the purpose of this investigation, it was more readily prepared by the condensation of ethyl malonate and *p*-toluidine, the operation being conducted as in the case of the anilide derivative. The *p*-toluidine dissolved readily in the ethyl malonate, much heat being absorbed. The product was pure, melting at  $250^\circ$ , and the yield 53 per cent. of the theoretical. *Malondi-p-tolylamide* is sparingly soluble in alcohol or ethyl acetate, but readily so in acetic acid; it was therefore recrystallised from a mixture of ethyl acetate and acetic acid, and obtained in the form of brilliant scales with a pearly lustre.

*Ethyl Malon-p-tolylamate*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ .—The residual alcoholic mother liquor from the preparation of malon-*p*-tolylamide deposited on evaporation large, prismatic crystals, which, after recrystallisation from alcohol and water, melted at  $86^\circ$ . By its solubility and appearance, the substance was identified with the malon-*p*-tolylamate prepared by Rügheimer and Hoffmann (*Ber.*, 1885, 18, 2975) from malon-*p*-tolylamic acid, but they do not give the melting point.

*isoNitrosomalondi-p-tolylamide*,  $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\cdot\text{C}\cdot\text{N}\cdot\text{OH}$ . — The malondi-*p*-tolylamide was suspended in chloroform, in which it was insoluble, and saturated at  $0^\circ$  with nitrosyl chloride; the solid dissolved completely, and the resulting yellow solution yielded on spontaneous evaporation the *isonitroso*-derivative in the form of a crystalline, pale yellow solid melting at  $170$ — $171^\circ$ . It is readily soluble in methyl alcohol, ethyl acetate, acetone, acetic acid, benzene, chloroform, or carbon tetrachloride, but less so in ethyl alcohol or toluene, and only sparingly so in ether or light petroleum. The recrystallised product consists usually of yellow scales or flattened needles melting at  $170$ — $171^\circ$ ; from a methyl alcohol solution, however, the product separates almost entirely in pure white needles, which, on being heated, change to a yellow colour at about  $150^\circ$  and melt at  $170$ — $171^\circ$ . Traces of the white isomeride are also formed on complete evaporation



of solutions in ethyl alcohol, ethyl acetate, acetone, or carbon tetrachloride :

0.1994 gave 23.9 c.c. moist nitrogen at  $23.5^{\circ}$  and 765 mm.  $N = 13.57$ .

$C_{17}H_{17}O_3N_3$  requires  $N = 13.52$  per cent.

The *potassium* salt,  $(CO \cdot NH \cdot C_7H_7)_2C:N \cdot OK$ , is a pale yellow, crystalline solid, deposited in the form of clusters of fine needles from a concentrated hot alcoholic solution :

0.3073 gave 0.0766  $K_2SO_4$ .  $K = 11.19$ .

$C_{17}H_{16}O_3N_3K$  requires  $K = 11.19$  per cent.

*Regeneration of the isoNitroso-derivative from the Potassium Salt.*—From aqueous solutions of the potassium salt, carbon dioxide precipitated the white isomeride, whilst dilute sulphuric or acetic acid precipitated the yellow.

The *ferrous* salt is thrown down as a dark blue precipitate, indistinguishable in appearance from the corresponding compound of *isonitroso*-malonanilide, when ferrous sulphate is added to an aqueous solution of the potassium salt.

*Acid Silver Salt*,  $(CO \cdot NH \cdot C_7H_7)_2C:N \cdot OAg, (CO \cdot NH \cdot C_7H_7)_2C:N \cdot OH$ .—This is obtained as a pale yellow, flocculent precipitate when silver nitrate solution is added to an alcoholic solution of the *isonitroso*-compound :

0.2750 gave 0.0414 Ag.  $Ag = 15.06$ .

$C_{34}H_{33}O_6N_6Ag$  requires  $Ag = 14.79$  per cent.

#### V. *Malonmono-p-tolylamide*, $C_7H_7 \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$ .

Thirty grams of ethyl malonate ( $1\frac{1}{4}$  mols.) and 15 grams of *p*-toluidine (1 mol.) were heated to gentle ebullition in a reflux apparatus for 12 hours, 100 c.c. of ammonia solution (sp. gr. 0.88) added to the cooled product, the flask corked, and the contents repeatedly shaken during two days. The semi-solid mass, when allowed to evaporate spontaneously, yielded 40 grams of a crystalline solid consisting of a mixture of 17 grams of malonamide, 1.5 grams of *p*-toluidine, 14 grams of malonmono-*p*-tolylamide, and 4.5 grams of malondi-*p*-tolylamide. These were readily separated by taking advantage of their difference in solubility.

The malonmono-*p*-tolylamide consisted of white, crystalline scales with a pearly lustre, readily soluble in alcohol and the ordinary organic solvents, and crystallising well from a mixture of water and alcohol (about 6 : 1). It melted at  $144^{\circ}$  with slight decomposition.

The substance contains half a molecular proportion of water of crystallisation, which it loses when dried at  $100^{\circ}$ , the crystals becoming dull and opaque :

0.4723 lost 0.0214  $\text{H}_2\text{O}$  at  $100^\circ$ .  $\text{H}_2\text{O} = 4.53$ .

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.47$  per cent.

The hydrated compound becomes strongly electrified by pressure or friction; the dehydrated compound has not this characteristic.

The anhydrous form of malonmono-*p*-tolylamide melts at  $163$ — $164^\circ$  with slight decomposition:

0.1935 gave 23.9 c.c. moist nitrogen at  $16.5^\circ$  and 765 mm.  $\text{N} = 14.46$ .

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{N} = 14.61$  per cent.

*isoNitrosomalonmono-p-tolylamide*,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{N} \cdot \text{OH}$ —A quantitative yield of the *isonitroso*-derivative was obtained from the amide by suspending it in chloroform and saturating it at  $0^\circ$  with nitrosyl chloride; the solid did not appreciably pass into solution, but changed in appearance from white to yellow. On spontaneous evaporation of the chloroform, a pale yellow, crystalline residue was obtained, which was the *isonitroso*-derivative. It dissolves readily in alcohol or ethyl acetate, crystallising from a hot solution of the latter in the form of brilliant, prismatic, lemon-yellow crystals melting at  $183^\circ$  with slight decomposition. The white isomeride of this compound has not yet been isolated; from solutions in any of the ordinary organic solvents only the yellow form is obtained:

0.1694 gave 28 c.c. moist nitrogen at  $18.5^\circ$  and 758 mm.  $\text{N} = 19.00$ .

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$  requires  $\text{N} = 19.03$  per cent.

The *isonitroso*-derivative is soluble in alkali containing a little alcohol, the alkali salt separating on evaporation in the form of needle-shaped crystals of a deeper yellow colour than the *isonitroso*-compound.

*Regeneration of the isoNitroso-derivative from the Potassium Salt.*—The potassium salt of *isonitrosomalonmono-p-tolylamide* is very readily soluble in water, forming a solution of a deep yellow colour. When this solution is treated with carbon dioxide or sulphuric or acetic acid, it becomes perfectly colourless, and from the clear, colourless liquid the *isonitroso*-derivative slowly separates in the form of the characteristic yellow prisms. This result is of especial interest as serving to show that although the white isomeride of this compound cannot be separated in the solid form it does exist in acidified aqueous solutions.

*Ferrous Salt.*—A solution of the alkali salt gives, with ferrous sulphate, an intense bluish-purple coloration and precipitate. The shade of colour of the ferrous salt is interesting, being intermediate between the deep blue of the *isonitrosomalondi-p-tolylamide* compound, and the violet colour of the *isonitrosomalonamide* salt, and shows that the colour is influenced by the nature of the radicles replacing the hydrogen of the amido-groups.

VI. *Malondi-o-tolylamide*,  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$ .

*Malondi-o-tolylamide* was made by the same method as that used in obtaining the *p*-tolylamide, *o*-toluidine being substituted for *p*-toluidine. The condensation was effected much more quickly and completely than in the case of the *para*-compound. The product was a white, crystalline solid melting at  $193^\circ$ , and the yield 71 per cent. of the theoretical. It was sparingly soluble in alcohol or ethyl acetate, but readily so in glacial acetic acid. When recrystallised from a mixture of ethyl acetate and glacial acetic acid, it was obtained in the form of long, silky needles with a pearly lustre and melted at  $193^\circ$ :

0.2303 gave 19.4 c.c. moist nitrogen at  $19^\circ$  and 780 mm.  $\text{N} = 9.94$ .  
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$  requires  $\text{N} = 9.94$  per cent.

*isoNitrosomalondi-o-tolylamide*,  $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}:\text{N}\cdot\text{OH}$ .—The conversion of the amide into the isonitroso-derivative is effected readily and quantitatively by the method employed in the case of the anilide and *p*-tolylamide compounds, namely, by saturating finely-powdered malondi-*o*-tolylamide suspended in chloroform with nitrosyl chloride at  $0^\circ$ . *isoNitrosomalondi-o-tolylamide* is very readily soluble in all the ordinary organic solvents, and crystallises well from ethyl alcohol or light petroleum in the form of fine, bright yellow needles. The yellow variety is obtained from solutions of other solvents with the exception of methyl alcohol, which yields also the white variety in the form of tufts of white needles. The yellow isomeride melts at  $111^\circ$ , the white changes to the yellow at about  $75^\circ$  and melts at  $111^\circ$ :

0.2150 gave 24.7 c.c. moist nitrogen at  $20.5^\circ$  and 779.5 mm.  $\text{N} = 13.46$ .  
 $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3$  requires  $\text{N} = 13.52$  per cent.

The *potassium* salt,  $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}:\text{N}\cdot\text{OK}$ , is soluble in water and slightly so in alcohol, crystallising from a mixture of water and alcohol (2:1) in the form of thin needles of a rich yellow colour:

0.2645, dried at  $110^\circ$ , gave 0.0640  $\text{K}_2\text{SO}_4$ .  $\text{K} = 10.86$ .  
 $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_3\text{K}$  requires  $\text{K} = 11.19$  per cent.

*Regeneration of the isoNitroso-derivative from the Potassium Salt*.—Carbon dioxide or dilute sulphuric or acetic acid precipitates the yellow isomeride from aqueous solutions of the potassium salt.

The *ferrous* salt is thrown down as a precipitate of a rich dark blue colour when ferrous sulphate is added to a solution of the potassium salt.

*Ethyl Malon-o-tolylamate*,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5$ .—The final alcoholic mother liquor from which the malondi-*o*-tolylamide had been



separated yielded on evaporation well-formed, prismatic crystals in stellate clusters. When recrystallised from alcohol and water, these melted at  $78^{\circ}$ , and were identified as ethyl malon-*o*-tolylamate originally prepared by Rügheimer and Hoffmann (*Ber.*, 1885, 18, 2975) from malon-*o*-tolylamic acid, who give  $73-74^{\circ}$  as the melting point. The substance was prepared in larger quantity by heating a mixture of ethyl malonate and *o*-toluidine in molecular proportion. A mixture of 5 grams of malondi-*o*-tolylamide and 16 grams of ethyl malon-*o*-tolylamate was obtained from 16 grams of ethyl malonate. The two were readily separated by extraction with boiling ether, in which the ethyl malon-*o*-tolylamate is soluble.

*Ethyl isonitrosomalon-*o*-tolylamate*,  $C_7H_7 \cdot NH \cdot CO \cdot C(CO_2C_2H_5)_2 \cdot N \cdot OH$ .—By the action of nitrosyl chloride on ethyl malon-*o*-tolylamate in chloroform solution at  $0^{\circ}$ , a quantitative yield of the *isonitroso*-derivative is obtained in the form of tufts of yellow needles. The compound is very readily soluble in all the ordinary organic solvents, and does not crystallise well from any of them. It separates, however, from a mixture of alcohol and water in tufts of beautiful, long, pale yellow needles melting at  $140-141^{\circ}$ :

0.2448 gave 23.1 c.c. moist nitrogen at  $16.5^{\circ}$  and 778 mm.  $N = 11.23$ .

$C_{12}H_{14}O_4N_2$  requires  $N = 11.22$  per cent.

The compound is soluble in aqueous potash, forming a bright yellow solution, the colour changing to a rich bluish-purple on the addition of ferrous sulphate.

## VII. *Malondi- $\alpha$ -naphthylamide*, $CH_2(CO \cdot NH \cdot C_{10}H_7)_2$ .

Seventeen grams of  $\alpha$ -naphthylamine (2 mols.) and 10 grams of ethyl malonate (1 mol.) were heated to gentle ebullition in a reflux apparatus for 5 or 6 hours; on cooling, the contents of the flask became solid. After grinding the product with alcohol, filtering, and washing, 16.5 grams of the amide were obtained, or 75 per cent. of the theoretical.

Malondi- $\alpha$ -naphthylamide is very sparingly soluble in alcohol, chloroform, ethyl acetate, or benzene, but fairly so in toluene and in glacial acetic acid. It crystallises from acetic acid in tufts of pale red needles melting at  $225^{\circ}$ :

0.3216 gave 21.8 c.c. moist nitrogen at  $18^{\circ}$  and 763 mm.  $N = 7.86$ .

$C_{23}H_{18}O_2N_2$  requires  $N = 7.92$  per cent.

*isoNitrosomalondi- $\alpha$ -naphthylamide*,  $(CO \cdot NH \cdot C_{10}H_7)_2C \cdot N \cdot OH$ .—Malondi- $\alpha$ -naphthylamide is completely converted into the *isonitroso*-derivative when suspended in ethyl acetate, xylene, or toluene, and saturated with nitrosyl chloride at the temperature of melting ice. After evaporating the product to dryness and washing with alcohol, the

isonitroso-derivative is obtained as a dark orange, crystalline solid, sparingly soluble in ethyl acetate or glacial acetic acid, but more soluble in alcohol, and readily so in benzene, toluene, or xylene; it crystallises from toluene in bright orange prisms and melts at  $184^{\circ}$ :

0.2513 gave 23.5 c.c. moist nitrogen at  $18.7^{\circ}$  and 752 mm.  $N = 10.68$ .

$C_{23}H_{17}O_3N_2$  requires  $N = 10.98$  per cent.

The potassium salt,  $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot OK$ , crystallises in thin orange-yellow needles, and is sparingly soluble in water, but dissolves readily in alcohol or ethyl acetate. For analysis, it was crystallised from alcohol:

0.3128, dried at  $120^{\circ}$ , gave 0.0637  $K_2SO_4$ .  $K = 9.14$ .

$C_{23}H_{16}O_3N_3K$  requires  $K = 9.28$  per cent.

#### VIII. Malondi- $\beta$ -naphthylamide, $CH_2(CO \cdot NH \cdot C_{10}H_7)_2$

The condensation of ethyl malonate and  $\beta$ -naphthylamine is readily effected by heating the substances in the requisite proportion in a reflux apparatus; the solid product separates from the boiling mixture as a crust, and the yield is 95 per cent. of the theoretical.

After washing with alcohol, the product is a white, crystalline powder which can be used in the preparation of the isonitroso-derivative without recrystallisation.

Malondi- $\beta$ -naphthylamide is sparingly soluble in alcohol, acetone, ethyl acetate, light petroleum, benzene, toluene, or xylene, crystallising from each of these solvents in long needles; it is more readily soluble in glacial acetic acid, crystallising from a boiling solution in white scales with a brilliant, pearly lustre. It melts at  $235^{\circ}$  to a yellow liquid and immediately solidifies to a yellow, crystalline solid which does not melt at  $300^{\circ}$ , but chars at the edges:

0.3198 gave 21.9 c.c. moist nitrogen at  $19^{\circ}$  and 766 mm.  $N = 7.93$ .

$C_{23}H_{18}O_2N_2$  requires  $N = 7.92$  per cent.

iso-Nitrosomalondi- $\beta$ -naphthylamide,  $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot OH$ .—The insoluble nature of malondi- $\beta$ -naphthylamide made it difficult to find a medium in which the isonitroso-derivative could be produced by the action of nitrosyl chloride. Preliminary experiments with most of the organic solvents showed that in ethyl acetate or toluene the reaction was more complete than in any other solvent; the products obtained in the two cases were different, and in neither case was a good yield obtained. The product obtained by the use of toluene was a pale yellow, crystalline solid melting with slight decomposition at  $219^{\circ}$ . It was sparingly soluble in alcohol, ethyl acetate, or chloroform, but more readily so in benzene, toluene, or acetic acid. For analysis,

it was recrystallised from acetic acid, from which it separated in pale yellow, shining plates melting at  $221^{\circ}$ :

0.2380 gave 21.8 c.c. moist nitrogen at  $17.2^{\circ}$  and 765 mm.  $N = 10.69$ .

$C_{23}H_{17}O_3N_3$  requires  $N = 10.98$  per cent.

The *potassium* salt is slightly soluble in water and readily so in alcohol, crystallising from moist alcohol in the form of wart-like tufts of very pale yellow, slender needles.

The *ferrous* salt is a dark blue solid precipitated by ferrous sulphate from a solution of the potassium salt.

The *acetyl* derivative,  $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot O \cdot CO \cdot CH_3$ , crystallises from alcohol or ethyl acetate in thin, pale green, silky needles, melting with decomposition at  $179^{\circ}$ . The colour appears to be due to the trace of an impurity, for it becomes less intense with each recrystallisation:

0.2422 gave 20 c.c. moist nitrogen at  $16^{\circ}$  and 744 mm.  $N = 9.42$ .

$C_{25}H_{19}O_4N_3$  requires  $N = 9.90$  per cent.

*Chlorinated isoNitrosomalondi- $\beta$ -naphthylamide*,  $C_{23}H_{16}O_3N_3Cl$ .—When nitrosyl chloride acts on malondi- $\beta$ -naphthylamide suspended in ethyl acetate, the product is a pale yellow, crystalline powder from which boiling ethyl acetate extracts a bright yellow solid crystallising in shining plates and melting at  $202^{\circ}$ . The melting point is not changed by recrystallising the substance from (1) a mixture of ethyl acetate and acetic acid, or (2) toluene. When heated on oxidised copper wire, the compound imparts a green colour to the flame, and therefore contains chlorine. Analyses of two different specimens of the substance showed it to be a chlorinated *isonitrosomalondi- $\beta$ -naphthylamide*:

I. 0.2130 gave 19.3 c.c. moist nitrogen at  $20.5^{\circ}$  and 748 mm.  $N = 10.17$ .

II. 0.2446 „ 21.5 c.c. „ „  $17^{\circ}$  „ 757 mm.  $N = 10.16$ .

$C_{23}H_{16}O_3N_3Cl$  requires  $N = 10.09$  per cent.

The position of the chlorine atom in this compound was not investigated. The potassium salt is yellow, and yields a dark blue, insoluble ferrous salt when mixed in solution with ferrous sulphate.

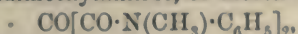
IX. *isoNitrosomalondimethylanilide*,  $[CO \cdot N(CH_3) \cdot C_6H_5]_2C:N \cdot OH$ .

*isoNitrosomalondimethylanilide* is prepared by the action of nitrosyl chloride on malondimethylanilide; it crystallises with one molecular proportion of methyl alcohol, melts at  $109^{\circ}$ , and gives the yellow coloration with alkalis, and the deep purple colour with ferrous sulphate, which is characteristic of this group of oximes. The acetyl



derivative melts at  $130^{\circ}$ , the benzoyl derivative at  $157-158^{\circ}$ , and the ethyl ether at  $138^{\circ}$ .

In addition to the normal reaction between malondimethylanilide and nitrosyl chloride, there is a further reaction whereby an isomeride of isonitrosomalondimethylanilide is obtained together with the corresponding ketonic compound. Up to the present, the conditions under which the reaction proceeds thus abnormally have not been determined and a full account of this part of the work is reserved for a later paper dealing with the tetra-substituted derivatives of the oxime of mesoxamide. It may, however, be stated that the ketone corresponding with isonitrosomalondimethylanilide, or mesoxdimethylanilide,



crystallises in well-developed, prismatic crystals of a deep orange colour and melts at  $172^{\circ}$ ; it yields the normal isonitroso-derivative melting at  $109^{\circ}$  by the action of hydroxylamine both in acid and alkaline solution. The isomeric isonitrosomalondimethylanilide, ( $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_2$ ), crystallises in tufts of thin, flattened needles of a pale yellow colour melting at  $192^{\circ}$ ; the ethyl ether melts at  $168^{\circ}$ , and the acetyl derivative at  $223^{\circ}$ . It forms colourless, crystalline alkali salts which are very soluble in water, the solutions give a rich purple-crimson colour with ferric chloride. From aqueous solutions of the alkali salts, mineral acids precipitate a well-defined colourless, crystalline, compound which melts at  $256^{\circ}$  and has not yet been identified; on treatment with sodium ethoxide, it regenerates the original sodium salt, from which, through the silver salt, the ethyl ether melting at  $168^{\circ}$  is obtained.

#### X. Behaviour of $\alpha$ -Oximinoketones with Ferrous Sulphate and Alkali.

(1) *isoNitrosoacetone* forms a bright yellow alkali solution (Meyer and Züblin, *Ber.*, 1878, 11, 695); the addition of ferrous sulphate produces an intense blue coloration.

(2) *Ethyl isonitrosoacetoacetate* gives a yellow colour with soda (Jovitschitsch, *Ber.*, 1895, 28, 2683); on the further addition of ferrous sulphate, a deep blue coloration is produced.

(3) *Ethyl isonitrosobenzoylacetate* dissolves readily in alkalis with a yellow colour (Perkin, *Trans.*, 1885, 47, 244); on the addition of ferrous sulphate, a deep indigo-blue precipitate is thrown down.

(4) *isoNitrosoacetylacetone* is readily soluble in alkalis giving a bright yellow colour (Zanetti, *Ber.*, 1893, 26, Ref. 598); the addition of a drop of ferrous sulphate produces an intense blue coloration.

(5)  $\gamma$ -*isoNitroso- $\beta$ -ketopentane* melts at  $53-55^{\circ}$  and is soluble in alkalis with a yellow colour (Meyer and Züblin, *Ber.*, 1878, 11, 323). The

melting point was found to be 58—59°, and the addition of ferrous sulphate to the yellow alkaline solution produced a deep blue coloration.

(6) iso*Nitrosocamphor* is soluble in alkalis with a yellow colour (Claisen and Manasse, *Annalen*, 1893, 274, 77); the addition of ferrous sulphate develops a deep blue coloration.

(7 and 8)  $\alpha$ -*Benzilmonoxime* and  $\beta$ -*benzilmonoxime* dissolved readily in alkalis giving deep yellow solutions (Auwers and Meyer, *Ber.*, 1889, 22, 540). On the further addition of ferrous sulphate, the solution of the  $\alpha$ -oxime gave a Prussian blue precipitate, which, when dried, dissolved readily in benzene forming a deep blue solution. The alkali solution of the  $\beta$ -oxime, on the other hand, gave only the green precipitate of ferrous hydroxide.

(9) iso*Nitrosophenylisoxazolone* dissolves in alkalis with a rose-red colour (Claisen and Zedel, *Ber.*, 1891, 24, 140); the addition of ferrous sulphate throws down a dark greenish-blue precipitate.

(10) iso*Nitrosomethylisoxazolone* dissolves in alkalis with a red colour (Nussberger, *Ber.*, 1892, 25, 2157); the colour changes to a deep chocolate-brown on the addition of ferrous sulphate.

#### XI. Behaviour of Dioximes with Ferrous Sulphate and Alkali

(1)  $\alpha$ -*Benzildioxime* (Auwers and Meyer, *Ber.*, 1888, 21 793) is sparingly soluble in alkalis yielding solutions of a faint yellow colour, which changes to a rich purple on the addition of ferrous sulphate. Attempts to prepare the potassium salt were unsuccessful, as it is rapidly hydrolysed by hot water or by methyl or ethyl alcohol.

The *ferrous* salt was obtained in the form of a finely-divided precipitate by adding freshly prepared ferrous sulphate solution to a solution of the oxime in aqueous potash; it was filtered, washed with water until the washings were no longer alkaline, and dried in the desiccator. The dry mass was almost black and had a peculiar shining appearance, not unlike that of coal. For the purpose of analysis, it was finely powdered and dried at 100° until the weight was constant:

0.4574 gave 0.1211  $\text{Fe}_2\text{O}_3$  and 0.0107  $\text{K}_2\text{SO}_4$ . Fe = 18.53; K = 1.05.

0.5410 „ 0.1460  $\text{Fe}_2\text{O}_3$  „ 0.0132  $\text{K}_2\text{SO}_4$ . Fe = 18.89; K = 1.09.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Fe}$  requires Fe = 19.04; K = 0 per cent.

Before the second analysis was made, the salt was extracted several times with boiling water and then with alcohol, but although the results serve to show that the purple colour obtained by the interaction of  $\alpha$ -benzildioxime with ferrous sulphate and an alkali is due to the formation of a coloured ferrous salt, the latter was not isolated in a pure form.

(2) *β-Benzildioxime* (Auwers and Meyer, *Ber.*, 1888, 21, 794) dissolves in alkalis with a pale yellow colour; the solution gives with ferrous sulphate only a ferrous hydroxide precipitate.

(3) *γ-Benzildioxime* (Beckmann and Küster, *Annalen*, 1893, 274, 19). The pale yellow sodium salt dissolves readily in water, and on adding ferrous sulphate solution a precipitate is formed of a dull purple colour, changing rapidly to brown.

(4) *Syn-dxime* of *ethyl isonitrosoacetoacetate* dissolves in alkalis forming a colourless solution (Ceresole and Kückert, *Ber.*, 1884, 17, 821); on the further addition of ferrous sulphate, a deep purple coloration is developed.

(5) *Methylethylglyoxime* (Schramm, *Ber.*, 1883, 16, 180) is sparingly soluble in alkalis giving a pale yellow solution which changes to a deep reddish-brown on the addition of ferrous sulphate.

*Ethylnitrolic acid* gives an orange-yellow colour with alkalis (Meyer and Constam, *Annalen*, 1882, 214, 329); the colour changes to a deep chocolate brown on the addition of ferrous sulphate.

The colour reactions with ferrous sulphate described in this and in the preceding section form very delicate tests for the respective oximes.

My sincere thanks are due to Professor Tilden for the opportunities afforded to me for carrying out this investigation and for much advice and encouragement received during its progress.

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## V.—The Vapour Pressures and Boiling Points of Mixed Liquids. Part II.

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

IN a paper by one of us under the same title (*Trans.*, 1902, 81, 752), reference was made to Guthrie's conclusion that if we could find two liquids showing no volume change or heat change on mixing, the vapour pressures should be expressed by a formula which reduces to  $P = \frac{pP_A + (100 - p)P_B}{100}$ , where  $P$ ,  $P_A$ , and  $P_B$  are

the vapour pressures of the mixture and of the two components  $A$  and  $B$  respectively at the same temperature, and  $p$  is the percentage by weight of the liquid  $A$ . In other words, the relation between the



vapour pressure and the percentage composition by weight should be represented by a straight line.

The conclusion of van der Waals was also alluded to, that if the critical pressures of the two liquids are equal, and if the relation suggested by Galitzine and by Berthelot,  $a_{1,2} = \sqrt{a_1 a_2}$  holds good, the relation between vapour pressures and molecular composition should be represented by a straight line, or the equation already given should hold good if  $p$  is the molecular percentage of  $A$ .

Mention should also have been made of a series of papers by Speyers on boiling point curves (*Amer. J. Sci.*, 1900, [iv], 9, 341), and on the molecular weights of liquids (*J. Amer. Chem. Soc.*, 1899, 21, 282; *J. Physical Chem.*, 1898, 2, 347, 362). Making use of the equation

$\frac{n_1}{n_2 + n_1} = \frac{p - p'}{p}$ , where  $n_1$  and  $n_2$  are the number of gram-molecules of the constituents,  $p$  is the vapour pressure of the second constituent when pure, and  $p'$  the partial pressure of the second constituent after the first has been added, Speyers arrives at the conclusion that when the molecular weights of both constituents are normal, the partial pressures of each, and the total vapour pressures of the mixtures when severally plotted against the molecular percentages of one constituent, give straight lines.

In part I of this series of papers, it was proved that so far as chlorobenzene and bromobenzene are concerned, the statement of van der Waals is correct, but it does not follow that the formula  $P = \frac{pP_A + (100 - p)P_B}{100}$  is applicable only to pairs of liquids which have the same critical pressure.

On the other hand, the statement of Speyers is certainly too general, for cases have been observed by Lehfeldt (*Phil. Mag.*, 1898, [v], 46, 42) and by Zawidski (*Zeit. physikal. Chem.*, 1900, 35, 129) of mixtures of liquids of normal molecular weight, the vapour pressures of which are not given by the above formula.

It seemed of interest therefore to investigate the behaviour of liquids which, although closely related chemically, have different critical pressures, and mention should first be made of the determination by Zawidski (*loc. cit.*) of the vapour pressures of mixtures of ethylene and propylene dibromides. In this case, he found that not only the vapour pressures of the mixtures, but also the partial pressures of the constituents, when mapped against the molecular percentages of the constituents, gave straight lines. But the critical pressures of these results were not known, and it is very doubtful whether the composition of the mixtures was heated to their critical points without decomposition. In a pure form, a number of pairs of closely related liquids have been examined: (1) benzene and ethyl propionate, (2) toluene and ethylbenzene,

(3) *n*-hexane and *n*-octane, (4) benzene and toluene, and, in addition, carbon tetrachloride and benzene, which, although not closely related, are of interest as they have been the subject of investigation by Linebarger (*J. Amer. Chem. Soc.*, 1895, 17, 615, 690), Löhfeldt (*loc. cit.*), and Zawidski (*loc. cit.*), and as the results obtained by the first of these workers differ notably from those of the others.

The critical pressures of the above liquids are as follows:

|                         | Crit. press.<br>in atm. | $\Delta$<br>atm. |                                 | Crit. press.<br>in atm. | $\Delta$<br>atm. |
|-------------------------|-------------------------|------------------|---------------------------------|-------------------------|------------------|
| Ethyl acetate.....      | 38.00                   | 4.83             | <i>n</i> -Hexane .....          | 29.62                   | 4.98             |
| Ethyl propionate. 33.17 |                         |                  | <i>n</i> -Octane .....          | 24.64                   |                  |
| Toluene .....           | 41.6*                   | 3.5              | Toluene .....                   | 41.6*                   | 8.5              |
| Ethylbenzene ... 38.1*  |                         |                  | Benzene.....                    | 50.1*                   |                  |
|                         |                         |                  |                                 | 47.88†                  |                  |
|                         |                         |                  | Carbon tetra-<br>chloride ..... | 44.97                   | 2.91             |

In all cases, there is a marked difference between the critical pressures, so that the influence of this constant can be thoroughly investigated.

### I. Ethyl Acetate and Ethyl Propionate.

As the quantity of purified material left from previous researches on the esters was insufficient for our purpose, a larger quantity of each was obtained from Kahlbaum. The liquids were thoroughly dried with phosphoric oxide, distilled over the same dehydrating agent, and fractionated through the 18 column dephlegmator.

#### Ethyl acetate.

#### Ethyl propionate.

#### Boiling Points.

| Temperature        |           |                     | Temperature |                    |                     |
|--------------------|-----------|---------------------|-------------|--------------------|---------------------|
| Pressure.          | observed. | corr. to<br>760 mm. | Pressure.   | observed.          | corr. to<br>760 mm. |
| 758.4 mm.          | 77.10°    | 77.17°              | 744.45 mm.  | 98.44°             | 99.10°              |
| 744.45 "           | 76.57     | 77.19               | 753.45 "    | 98.86              | 99.14               |
|                    |           |                     | 761.2 "     | 99.15              | 99.10               |
|                    | Mean      | 77.18               | 761.4 "     | 99.16              | 99.10               |
| Previous results * |           | 77.15               | 762.25 "    | 99.23              | 99.14               |
|                    |           |                     |             | Mean               | 99.12               |
|                    |           |                     |             | Previous results ‡ | 99.0                |

\* Altschul (*Zeit. physikal. Chem.*, 1893, 11, 590).

† Young (*Trans.*, 1889, 55, 486).

As the critical pressures of toluene and ethylbenzene have been determined by Altschul, it seems best to give his value for that of benzene in the comparison with toluene.

‡ *Trans.*, 1893, 63, 1191.

*Sp. gr. at 0°/4°.*

|                   |         |                   |         |
|-------------------|---------|-------------------|---------|
|                   | 0.92446 |                   | 0.91251 |
| Previous results* | 0.92436 | Previous results* | 0.91240 |

*Change of Volume on Mixing.*

A mixture in approximately molecular proportion was then made, and its specific gravity at 0°/4° determined.

| Molecular composition. |              | Sp. gr. at 0°/4° .....   | 0.91785 |
|------------------------|--------------|--------------------------|---------|
| Ethyl acetate .....    | 49.87        | Volume of a gram obs.    | 1.08950 |
| Ethyl propionate ..... | 50.13        | Volume of a gram calc.   | 1.08934 |
|                        | <hr/> 100.00 |                          |         |
|                        |              | Difference.....          | 0.00016 |
|                        |              | Percentage difference... | 0.015   |

*Change of Temperature on Mixing.*

The method was the same as that employed in the case of chlorobenzene and bromobenzene (Trans., 1902, 81, 772). The volume of the mixture was in all cases about 20 c.c. :

|                         |                       |             |
|-------------------------|-----------------------|-------------|
| Molecular composition : | Ethyl acetate .....   | 50.1        |
|                         | Ethyl propionate..... | 49.9        |
|                         |                       | <hr/> 100.0 |

|            | Ethyl acetate. | Ethyl propionate. | Mean.  | Mixture. | Δ.      |
|------------|----------------|-------------------|--------|----------|---------|
| Temp. .... | 20.53°         | 20.70°            | 20.62° | 20.60°   | - 0.02° |

It will be seen that there is an exceedingly slight expansion and absorption of heat on mixing.

*Boiling Points of Mixtures.*

The apparatus employed for the determination of the boiling points of mixtures was the same as that previously used for chlorobenzene and bromobenzene. The total volume of the liquid and vapour phases was very nearly 200 c.c., that of the liquid was in each case approximately 125 c.c. As with mixtures of chlorobenzene and bromobenzene, the temperature of the liquid was taken into account as well as that of the vapour. It was found that for each mixture there was a nearly constant difference between the two temperatures. The mean value of this constant was subtracted from each temperature reading of the liquid in order to eliminate the effect due to superheating and to get a second observation of the true boiling point. The mean of the direct and indirect readings was taken in each case as correct.

\* Trans., 1893, 63, 1191.



*Boiling Points of Mixtures of Ethyl Acetate and Ethyl Propionate.*

Molecular percentages of ethyl propionate.

| 25.01.           |        | 50.00.           |        | 74.62.           |        |
|------------------|--------|------------------|--------|------------------|--------|
| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  |
| 661.1            | 76.94° | 667.1            | 82.06° | 663.6            | 87.47° |
| 673.6            | 77.52  | 678.0            | 82.56  | 676.4            | 88.06  |
| 684.9            | 78.02  | 689.2            | 83.07  | 687.5            | 88.56  |
| 695.1            | 78.50  | 701.4            | 83.61  | 698.7            | 89.07  |
| 705.3            | 78.92  | 712.7            | 84.14  | 710.1            | 89.58  |
| 717.3            | 79.43  | 722.3            | 84.54  | 720.7            | 90.09  |
| 729.6            | 79.96  | 734.2            | 85.06  | 731.1            | 90.54  |
| 743.9            | 80.56  | 745.2            | 85.53  | 741.5            | 90.98  |
| 754.2            | 81.01  | 760.0            | 86.13  | 749.1            | 91.34  |
| 760.2            | 81.22  | 772.1            | 86.64  | 758.4            | 91.69  |
| 771.8            | 81.70  | 785.4            | 87.16  | 769.1            | 92.29  |
| 781.9            | 82.13  | 798.7            | 87.68  | 782.1            | 92.69  |
| 793.2            | 82.58  | 811.3            | 88.20  | 794.6            | 93.22  |
| 806.3            | 83.07  | 823.4            | 88.66  | 806.0            | 93.68  |
| 819.3            | 83.61  | 836.9            | 89.17  | 817.9            | 94.17  |
| 832.7            | 84.10  | 849.4            | 89.65  | 830.5            | 94.69  |
| 846.4            | 84.60  | —                | —      | 843.5            | 95.18  |

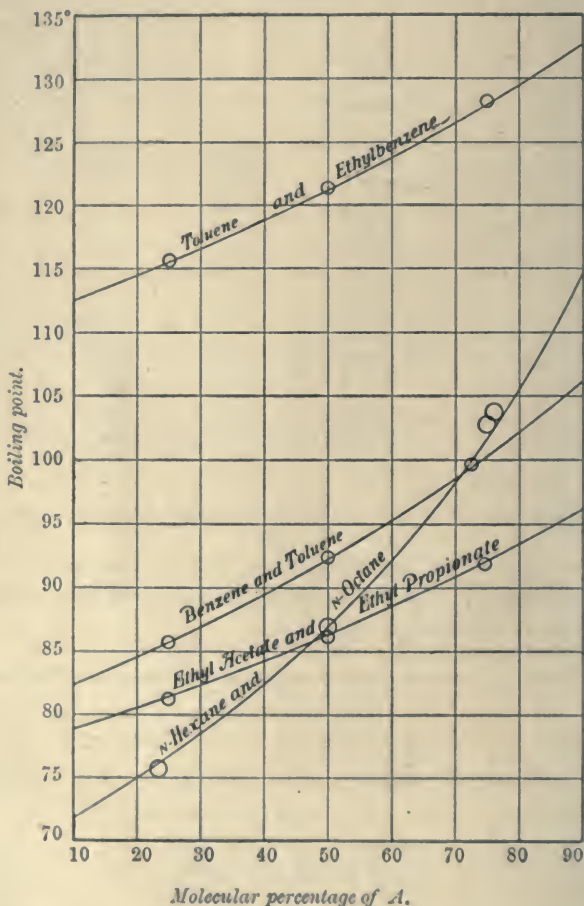
The logarithms of the pressures were in each case mapped against the temperatures and the boiling points under pressures of 700, 760, and 820 mm. read from the curves.

| Pressure,<br>mm. | Molecular percentages of ethyl propionate. |        |        |
|------------------|--|--------|--------|
|                  | 25.01.                                     | 50.00. | 74.62. |
| 700              | 75.69°                                     | 83.55° | 89.15° |
| 760              | 81.26                                      | 86.15  | 91.82  |
| 820              | 83.61                                      | 88.52  | 94.24  |

Data for the theoretical boiling point curves were calculated by means of the formula  $p = \frac{100(P_B - P)}{P_B - P_A}$ , where  $p$  is the molecular percentage of the liquid A,  $P_A$  and  $P_B$  are the vapour pressures of the components A and B, and  $P$  is the pressure under which the mixture is boiling. The molecular percentage of ethyl propionate for values

700, 760, and 820 of  $P$  were then calculated from the formula at a series of even temperatures and the theoretical isobars so obtained. It was found in every case that the deviations of the points representing the observed boiling points from the curves were practically the

FIG. 1.



same at the three pressures, and it seems therefore sufficient to give only the curve for normal pressures. These theoretical curves with the points representing the actual observations are given in Fig. 1.

For the calculation of  $P_A$  and  $P_B$ , Biot's shorter formula  $\log p = a + ba'$ , was employed; the constants for this formula are given below:

Ethyl acetate.  
 $a = 4.85820$   
 $\log b = (-)0.4446305$   
 $\log a = 1.99685012$   
 $t = t^\circ - 30$

Ethyl propionate.  
 $a = 4.86079$   
 $\log b = (-)0.4127340$   
 $\log a = 1.99703245$   
 $t = t^\circ - 60$

The vapour pressures of the two pure liquids at the observed boiling points of the mixtures under the three pressures were then calculated by means of Biot's formula and then from the equation  $P = \frac{pP_A + (100 - p)P_B}{100}$  the theoretical values of  $P$  were obtained.

In the following table are given the vapour pressures of ethyl acetate and ethyl propionate at the observed boiling points of the mixtures, and the values of  $P$  calculated from the above formula :

| Molecular<br>percentage<br>of ethyl<br>propionate. | Temp.  | Vapour pressures at $t^\circ$<br>from Biot's formula. |                   | $P$ calc. | $P$ observed. | $\Delta$ . |
|--|--------|---|-------------------|-----------|---------------|------------|
|  |        | Ethyl<br>propionate.                                  | Ethyl<br>acetate. |           |               |            |
| 25.01  | 78.69° | 384.0   | 799.3             | 695.4     | 700           | -4.6       |
| 50.00  | 83.55  | 455.7   | 934.2             | 694.9     |               | -5.1       |
| 74.62  | 89.15  | 551.2   | 1110.6            | 693.2     |               | -6.8       |
|  |        |   | Mean...           | 694.5     |               | -5.5       |
| 25.01  | 81.26  | 420.6   | 868.5             | 756.5     | 760           | -3.5       |
| 50.00  | 86.15  | 498.2   | 1013.2            | 755.7     |               | -4.3       |
| 74.62  | 91.82  | 602.0   | 1203.2            | 754.6     |               | -5.4       |
|  |        |   | Mean...           | 755.6     |               | -4.4       |
| 25.01  | 83.61  | 456.6   | 935.9             | 816.0     | 820           | -4.0       |
| 50.00  | 88.52  | 539.7   | 1089.5            | 814.6     |               | -5.4       |
| 74.62  | 94.24  | 651.2   | 1291.9            | 813.8     |               | -6.2       |
|  |        |   | Mean...           | 814.8     |               | -5.2       |

The agreement is by no means so close as with chlorobenzene and bromobenzene, and the differences are beyond the limits of experimental error; they are also in the direction that might be anticipated from the slight expansion and fall of temperature on mixing the liquids. That the deviations, however, are really very small is perhaps better seen from the fact that the corresponding temperature differences at 760 mm. are only  $0.14^\circ$ ,  $0.18^\circ$ , and  $0.23^\circ$  respectively, and that those at the other pressures would not be much larger.



II. *Toluene and Ethylbenzene.*

Specimens of these substances were obtained from Kahlbaum and were fractionated, the toluene through the 18-column dephlegmator and the ethylbenzene through a 12-bulb "pear" still-head:

| <i>Toluene.</i>        |         |                     | <i>Ethylbenzene.</i> |         |                     |
|------------------------|---------|---------------------|----------------------|---------|---------------------|
| <i>Boiling points:</i> |         |                     |                      |         |                     |
| Temperature            |         |                     | Temperature          |         |                     |
| Pressure.              | obs.    | corr. to<br>760 mm. | Pressure.            | obs.    | corr. to<br>760 mm. |
| 774.7 mm.              | 111.35° | 110.67°             | 777.9 mm.            | 137.07° | 136.19°             |
| 770.2 „                | 111.17  | 110.70              | 774.7 „              | 136.92  | 136.20              |
| 756.9 „                | 110.34  | 110.48              | 763.2 „              | 136.37  | 136.21              |
| 762.4 „                | 110.66  | 110.51              | 739.1 „              | 135.20  | 136.25              |
| 758.4 „                | 110.51  | 110.58              | 759.0 „              | 136.09  | 136.14              |
| 757.0 „                | 110.54  | 110.68              | 762.7 „              | 136.24  | 136.11              |
| 749.05 „               | 110.15  | 110.65              |                      |         |                     |
| 751.7 „                | 110.25  | 110.63              |                      |         | Mean 136.18         |
| 747.7 „                | 110.05  | 110.62              |                      |         |                     |
| 758.0 „                | 110.52  | 110.61              |                      |         |                     |
|                        |         | Mean 110.62         |                      |         |                     |

*Sp. gr. at 0°/4°.*

0.88455

0.88457

It is somewhat remarkable that the tendency of the sp. gr. to be raised by increase of molecular weight should, in this case, be almost exactly counterbalanced by its tendency to be lowered by the greater influence of the larger alkyl group. Passing from benzene to toluene, the effect of the introduction of the alkyl group is so great that the sp. gr. actually falls considerably.

*Change of Volume on Mixing.*

| Molecular composition. |        | Sp. gr. at 0°/4° .....   |          |
|------------------------|--------|--------------------------|----------|
| Toluene .....          | 50.11  | Volume of a gram obs.... | 1.13012  |
| Ethylbenzene .....     | 49.89  | „ „ calc...              | 1.13050  |
|                        | 100.00 | Difference.....          | -0.00038 |
|                        |        | Percentage difference    | -0.034   |

*Change of Temperature on Mixing.*

| Molecular composition. |          |               |        |          |            |
|------------------------|----------|---------------|--------|----------|------------|
| Toluene                | .....    |               |        | 50.1     |            |
| Ethylbenzene           | .....    |               |        | 49.9     |            |
|                        |          |               |        | <hr/>    |            |
|                        |          |               |        | 100.0    |            |
| Temp.....              | Toluene. | Ethylbenzene. | Mean.  | Mixture. | $\Delta$ . |
|                        | 14.7°    | 14.65°        | 14.67° | 14.72    | + 0.05°    |

Unlike the two esters, toluene and ethylbenzene show a very slight contraction and rise of temperature when mixed together.

As a determination of the vapour pressures of toluene and of ethylbenzene had not been previously made, it was now carried out within the limits required for the present investigation. In the case of toluene, the pressure apparatus was used for determinations at 120° and higher temperatures :

*Vapour Pressures of Toluene.*

| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.   |
|------------------|--------|------------------|--------|------------------|--------|------------------|---------|
| 201.4            | 69.69° | 268.55           | 77.67° | 448.8            | 93.04° | 701.2            | 107.79° |
| 204.95           | 70.18  | 298.9            | 80.73  | 496.4            | 96.22  | 731.9            | 109.24  |
| 210.25           | 70.84  | 332.8            | 83.90  | 540.4            | 99.01  | 755.7            | 110.34  |
| 220.85           | 72.21  | 368.35           | 86.95  | 595.1            | 102.17 | 783.9            | 111.69  |
| 241.3            | 74.66  | 406.4            | 89.96  | 651.9            | 105.26 | 813.5            | 112.99  |

The following determinations were made with the pressure apparatus :

| Pressure,<br>mm. | Temp. | Pressure,<br>mm. | Temp. | Pressure,<br>mm. | Temp. |
|------------------|-------|------------------|-------|------------------|-------|
| 992              | 120°  | 1459             | 135°  | 2072             | 150°  |
| 1135             | 125   | 1646             | 140   | 2315             | 155   |
| 1289             | 130   | 1849             | 145   | —                | —     |

For the determinations of the vapour pressures of ethylbenzene, the boiling point apparatus was used throughout :

*Vapour Pressures of Ethylbenzene.*

| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.   | Pressure,<br>mm. | Temp.   |
|------------------|--------|------------------|--------|------------------|---------|------------------|---------|
| 121·2            | 78·93° | 231·85           | 96·86° | 456·8            | 118·08° | 750·2            | 135·62° |
| 123·95           | 79·52  | 257·15           | 99·90  | 499·3            | 121·06  | 786·8            | 137·43  |
| 134·3            | 81·60  | 284·15           | 102·93 | 546·6            | 124·25  | 829·1            | 139·44  |
| 150·65           | 84·74  | 313·65           | 105·98 | 596·5            | 127·30  | 871·5            | 141·29  |
| 163·15           | 87·80  | 346·9            | 109·11 | 648·6            | 130·32  | —                | —       |
| 188·05           | 90·87  | 381·0            | 112·13 | 684·8            | 132·24  | —                | —       |
| 209·45           | 93·96  | 417·45           | 115·12 | 724·4            | 134·36  | —                | —       |

The following table gives the vapour pressures of the two substances at intervals of 10° of temperature read from the curves, together with the values calculated from Biot's formula :

| Toluene. |                |         |        |            | Ethylbenzene. |                |       |            |
|----------|----------------|---------|--------|------------|---------------|----------------|-------|------------|
| Temp.    | Pressure.      |         |        | $\Delta$ . | Temp.         | Pressure.      |       | $\Delta$ . |
|          | From<br>curve. | Direct. | Biot.  |            |               | From<br>curve. | Biot. |            |
| 70°      | 203·7          | —       | 203·7  | 0          | 80°           | 126·4          | 126·4 | 0          |
| 80       | 289·9          | —       | 290·4  | +0·5       | 90            | 182·6          | 182·6 | 0          |
| 90       | 406·0          | —       | 405·6  | -0·4       | 100           | 257·6          | 257·9 | +0·3       |
| 100      | 555·9          | —       | 555·5  | -0·4       | 110           | 357·1          | 356·6 | -0·5       |
| 110      | 747·0          | —       | 747·0  | 0          | 120           | 482·7          | 483·3 | +0·6       |
| 120      | 990·8          | 992     | 987·2  | -3·6       | 130           | 641·5          | 642·9 | +1·4       |
| 130      | 1288·0         | 1289    | 1283·7 | -4·3       | 140           | 841·4          | 840·2 | -1·2       |
| 140      | 1646·0         | 1646    | 1643·9 | -2·1       |               |                |       |            |
| 150      | 2073·0         | 2072    | 2075·0 | +2·0       |               |                |       |            |

The boiling points of three mixtures of toluene and ethylbenzene were determined and the results are given in the following table :



*Boiling Points of Mixtures of Toluene and Ethylbenzene.*

## Molecular percentages of ethylbenzene.

| 25.02.           |         | 49.97.           |        | 75.00.           |         |
|------------------|---------|------------------|--------|------------------|---------|
| Pressure,<br>mm. | Temp.   | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.   |
| 657.05           | 111.00° | 682.2            | 117.5° | 662.9            | 123.26° |
| 677.5            | 111.51  | 685.3            | 117.67 | 671.9            | 123.71  |
| 688.4            | 112.07  | 690.3            | 117.93 | 682.1            | 124.27  |
| 698.15           | 112.54  | 699.0            | 118.36 | 692.4            | 124.83  |
| 707.5            | 113.04  | 705.6            | 118.74 | 702.6            | 125.41  |
| 717.7            | 113.53  | 712.3            | 119.04 | 712.3            | 125.92  |
| 727.25           | 114.00  | 719.6            | 119.42 | 723.8            | 126.43  |
| 737.45           | 114.45  | 728.75           | 119.90 | 734.15           | 126.92  |
| 744.95           | 114.89  | 737.95           | 120.35 | 743.65           | 127.43  |
| 754.05           | 115.32  | 746.3            | 120.76 | 753.55           | 127.89  |
| 764.45           | 115.81  | 752.65           | 121.01 | 762.3            | 128.31  |
| 776.05           | 116.35  | 761.7            | 121.51 | 771.85           | 128.78  |
| 789.2            | 116.91  | 772.15           | 122.02 | 779.55           | 129.15  |
| 800.95           | 117.44  | 783.85           | 122.53 | 790.8            | 129.66  |
| 811.55           | 117.93  | 796.25           | 123.11 | 801.45           | 130.18  |
| 822.05           | 118.41  | 808.75           | 123.67 | 812.65           | 130.66  |
| —                | —       | 822.15           | 124.25 | 824.7            | 131.23  |

The boiling points at 700, 760, and 820 mm. read from the curve are as follows :

| Pressure,<br>mm. | Molecular percentages of ethylbenzene. |         |         |
|------------------|--|---------|---------|
|                  | 25.02.                                 | 49.97.  | 75.00.  |
| 700              | 112.67°                                | 118.42° | 125.21° |
| 760              | 115.60                                 | 121.41  | 128.22  |
| 820              | 118.28                                 | 124.15  | 130.99  |

Data for the theoretical boiling point curves were calculated in the same manner as before and the deviations from the theoretical curve at 760 mm. are shown in Fig. 1 (p. 50). The constants for Biot's shorter formula are as follows :

$$\begin{aligned}
 &\text{Toluene} \\
 &a = 4.94942 \\
 &\log b = (-) 0.4216731 \\
 &\log a = \bar{1}.99738948 \\
 &t = t^\circ - 70
 \end{aligned}$$

$$\begin{aligned}
 &\text{Ethylbenzene} \\
 &a = 4.69593 \\
 &\log b = (-) 0.4139911 \\
 &\log a = \bar{1}.99723926 \\
 &t = t^\circ - 80
 \end{aligned}$$

It seems unnecessary to give full details of the calculation of the vapour pressures of the mixtures at the observed boiling points by means of the formula  $P = \frac{pP_A + (100 - p)P_B}{100}$ ; the final results only are given in the table below:

| Molecular percentages<br>of ethylbenzene. | Calculated pressures |       |       |
|---|----------------------|-------|-------|
|   | mm.                  | mm.   | mm.   |
| 25.02                                     | 701.5                | 762.8 | 821.3 |
| 49.97                                     | 703.6                | 763.5 | 824.3 |
| 75.00                                     | 705.4                | 765.5 | 824.8 |
|   | <hr/>                | <hr/> | <hr/> |
| Mean .....                                | 703.5                | 763.9 | 823.5 |
| Observed pressures                        | 700.0                | 760.0 | 820.0 |
|   | <hr/>                | <hr/> | <hr/> |
| $\Delta$                                  | +3.5                 | +3.9  | +3.5  |

The differences are rather smaller than with the two esters and are in the opposite direction, as are also the volume and temperature changes on mixing.

### III. *n*-Hexane and *n*-Octane.

The specimens used in former researches were available; they were redistilled over phosphoric oxide. The specific gravities at 0°/4° were redetermined, with the following results:

*Sp. gr. at 0°/4°.*

|            | <i>n</i> -Hexane. | <i>n</i> -Octane. |
|------------|-------------------|-------------------|
| New result | 0.67703           | 0.71854           |
| Old    ,,  | 0.67696*          | 0.71848†          |

### *Change of Volume on Mixing.*

|                               |                       |          |
|-------------------------------|-----------------------|----------|
| Molecular composition.        | Sp. gr. at 0°/4°..... | 0.70044  |
| [ <i>n</i> -Hexane..... 50.03 | Volume of a gram obs. | 1.13012  |
| <i>n</i> -Octane ..... 49.97  | ,,       calc.        | 1.13050  |
|                               | <hr/>                 | <hr/>    |
| 100.00                        | Difference            | -0.00038 |
|                               | Percentage difference | -0.034   |

### *Change of Temperature on Mixing.*

|                         |                        |       |
|-------------------------|------------------------|-------|
| Molecular composition : | <i>n</i> -Hexane.....  | 50.2  |
|                         | <i>n</i> -Octane ..... | 49.8  |
|                         | <hr/>                  | <hr/> |
|                         |                        | 100.0 |

|       | <i>n</i> -Hexane. | <i>n</i> -Octane. | Mean.  | Mixture. | $\Delta$ . |
|-------|-------------------|-------------------|--------|----------|------------|
| Temp. | 21.43°            | 21.58°            | 21.51° | 21.57°   | +0.06      |

\* Trans., 1895, 67, 1071.

† Trans., 1900, 77, 1145.

There is in this case very slight contraction and rise of temperature, but rather greater than with toluene and ethylbenzene.

*Boiling Points of Mixtures of n-Hexane and n-Octane.*

Molecular percentages of n-octane.

| 23.31.           |        | 50.00.           |        | 76.09.           |        | 74.99.           |        |
|------------------|--------|------------------|--------|------------------|--------|------------------|--------|
| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  |
| 657.3            | 70.97° | 664.0            | 82.28° | 657.0            | 98.61° | 658.7            | 97.66° |
| 670.7            | 71.60  | 672.2            | 82.65  | 667.8            | 99.15  | 670.9            | 98.26  |
| 682.7            | 72.24  | 684.8            | 83.26  | 677.8            | 99.70  | 684.7            | 99.04  |
| 690.9            | 72.87  | 694.6            | 83.87  | 688.8            | 100.21 | 698.1            | 99.69  |
| 710.0            | 73.45  | 708.9            | 84.39  | 701.0            | 100.78 | 712.2            | 100.44 |
| 724.0            | 74.08  | 718.9            | 85.05  | 711.3            | 101.32 | 728.4            | 101.15 |
| 738.3            | 74.73  | 731.4            | 85.54  | 723.9            | 102.03 | 742.9            | 101.90 |
| 748.3            | 75.10  | 745.8            | 86.21  | 736.6            | 102.66 | 756.4            | 102.50 |
| 760.6            | 75.65  | 760.4            | 86.96  | 747.1            | 103.16 | 767.4            | 103.12 |
| 773.0            | 76.17  | 771.6            | 87.42  | 754.4            | 103.44 | 778.1            | 103.59 |
| 784.4            | 76.54  | 782.8            | 87.96  | 766.0            | 104.03 | 789.1            | 104.10 |
| 796.2            | 77.13  | 794.9            | 88.47  | 778.7            | 104.63 | 800.5            | 104.64 |
| 807.6            | 77.75  | 807.6            | 89.00  | 791.0            | 105.20 | 811.9            | 105.15 |
| 819.6            | 78.14  | 820.4            | 89.55  | 804.0            | 105.75 | 823.1            | 105.64 |
| 831.5            | 78.79  | 833.7            | 90.14  | 817.1            | 106.32 | 834.1            | 106.14 |
| 842.5            | 79.10  | 846.4            | 90.79  | 829.9            | 106.89 | 845.7            | 106.65 |
| —                | —      | —                | —      | 843.6            | 107.56 | —                | —      |

The boiling points at 700, 760, and 820 mm., read from the curve are as follows :

| Pressure. | Molecular percentages of n-octane. |        |        |        |
|-----------|------------------------------------|--------|--------|--------|
|           | 23.31.                             | 50.00. | 74.99. | 76.09. |
| 700       | 73.02                              | 84.07  | 99.79  | 100.81 |
| 760       | 75.69                              | 86.93  | 102.74 | 103.74 |
| 820       | 78.13                              | 89.57  | 105.45 | 106.46 |

The difference between the observed and calculated boiling points with 75 molecules per cent. of n-octane was considerably greater than was expected, and it was thought possible that a little hexane might have been lost by evaporation during the transference from one vessel to another. A second mixture, of about the same composition, was therefore made up in the apparatus itself, and a second series of



determinations was carried out. The results, however, agreed well with the previous one.

The deviations of the observed boiling points from the theoretical curve are shown in Fig. 1 (p. 50).

The constants for Biot's formula  $\log p = a + ba^t + c\beta^t$  have already been given (Trans., 1895, 67, 1075; 1900, 77, 1146).

A comparison of pressures, similar to that given in previous cases, is shown in the table below:

| Molecular percentages<br>of <i>n</i> -octane. |                    | Calculated pressures. |       |       |       |
|---|--------------------|-----------------------|-------|-------|-------|
| 23.31   |                    | 692.3                 |       | 752.0 | 808.9 |
| 50.00   |                    | 698.8                 |       | 760.2 | 820.1 |
| 74.99   | 75.54              | 719.2                 | 721.4 | 781.6 | 842.0 |
| 76.09   |                    | 723.7                 |       | 785.3 | 846.4 |
|   | Mean               | 704.2                 |       | 765.6 | 824.4 |
|   | Observed pressures | 700.0                 |       | 760.0 | 820.0 |
|   | $\Delta$           | +4.2                  |       | +5.6  | 4.4   |

The individual deviations are somewhat large, but the mean of the calculated pressures are but little higher than the observed, as the differences are in opposite directions.

The mean deviations are in the direction that might be anticipated from the volume and temperature changes, but as the individual variations are so large, no great weight can be attached to this fact.

#### IV. *Benzene and Toluene.*

Specimens of these liquids, obtained from Kahlbaum, were fractionated and finally distilled over phosphoric oxide:

| <i>Benzene.</i>        |             |                     | <i>Toluene.</i> |             |                     |
|------------------------|-------------|---------------------|-----------------|-------------|---------------------|
| <i>Boiling point :</i> |             |                     |                 |             |                     |
| Pressure<br>mm.        | Temperature |                     | Pressure<br>mm. | Temperature |                     |
|                        | obs.        | corr. to<br>760 mm. |                 | obs.        | corr. to<br>760 mm. |
| 758.0                  | 80.09°      | 80.18°              | 758.0           | 110.59°     | 110.68              |

*Sp. gr. at 0°/4°.*

|                    |         |                   |         |
|--------------------|---------|-------------------|---------|
|                    | 0.90004 |                   | 0.88453 |
| Old result * ..... | 0.90006 | Previous specimen | 0.88455 |
| Jackson & Young †  | 0.90005 |                   |         |

\* Trans., 1899, 55, 488.

† Trans., 1898, 73, 923.

*Change of Volume on Mixing.*

| Molecular composition. |              | Sp. gr. at 0°/4" .....    | 0·89078 |
|------------------------|--------------|---------------------------|---------|
| Benzene .....          | 50·03        | Volume of a gram obs....  | 1·12261 |
| Toluene .....          | 49·97        | „ „ calc....              | 1·12080 |
|                        | <hr/> 100·00 | Difference .....          | 0·00181 |
|                        |              | Percentage difference ... | 0·1615  |

*Change of Temperature on Mixing.*

## Molecular composition

Benzene..... 49·95

Toluene ..... 50·05

---

100·00

|            | Benzene. | Toluene. | Mean  | Mixture. | Δ.     |
|------------|----------|----------|-------|----------|--------|
| Temp. .... | 19·00°   | 19·00°   | 19·00 | 18·55°   | - 0·45 |

The behaviour of benzene and toluene is similar to that of the two esters, but the expansion and fall of temperature are considerably greater.

*Boiling Points of Mixtures of Benzene and Toluene.*

## Molecular percentages of toluene.

| 24·94.           |        | 50·00.           |        | 72·46.           |        |
|------------------|--------|------------------|--------|------------------|--------|
| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  |
| 666·6            | 81·37° | 661·2            | 87·55° | 663·9            | 95·01° |
| 677·5            | 81·87  | 670·9            | 88·14  | 674·1            | 95·51  |
| 690·5            | 82·54  | 681·6            | 88·67  | 684·8            | 96·05  |
| 702·0            | 83·05  | 692·8            | 89·22  | 695·0            | 96·57  |
| 714·1            | 83·63  | 702·3            | 89·67  | 705·1            | 97·04  |
| 724·3            | 84·10  | 713·0            | 90·20  | 717·1            | 97·60  |
| 734·9            | 84·61  | 725·5            | 90·78  | 727·3            | 98·11  |
| 749·1            | 85·16  | 738·1            | 91·41  | 739·5            | 98·69  |
| 757·9            | 85·62  | 751·0            | 91·96  | 752·4            | 99·21  |
| 768·5            | 86·07  | 761·1            | 92·41  | 762·1            | 99·70  |
| 779·0            | 86·52  | 772·6            | 92·96  | 771·6            | 100·14 |
| 790·1            | 86·98  | 783·2            | 93·46  | 782·4            | 100·60 |
| 802·1            | 87·52  | 794·8            | 93·89  | 794·4            | 101·12 |
| 813·8            | 87·97  | 806·4            | 94·43  | 806·4            | 101·69 |
| 826·0            | 88·51  | 816·8            | 94·83  | 818·3            | 102·19 |
| 837·2            | 88·97  | 826·0            | 95·18  | 830·5            | 102·71 |

The following are the boiling points read from the curve at 700, 760, and 820 mm. :

| Pressure,<br>mm. | Molecular percentage of toluene. |        |        |
|------------------|----------------------------------|--------|--------|
|                  | 24.94.                           | 50.00. | 72.46. |
| 700              | 82.97°                           | 89.57° | 96.80° |
| 760              | 85.72                            | 92.38  | 99.63  |
| 820              | 88.23                            | 94.96  | 102.22 |

The deviations of the observed boiling points from the theoretical curve are shown in Fig. 1 (p. 50).

The constants for Biot's shorter formula for toluene have been already given; those for the larger formula for benzene are taken from a former paper (Trans., *loc. cit.*).

The usual comparison of pressures is given below :

| Molecular percentage<br>of toluene | Calculated pressures |        |        |
|------------------------------------|----------------------|--------|--------|
| 24.94                              | 699.88               | 760.57 | 819.90 |
| 50.00                              | 701.80               | 762.95 | 822.90 |
| 72.46                              | 703.96               | 764.55 | 823.60 |
| Mean.....                          | 701.88               | 762.69 | 822.13 |
| Observed pressures                 | 700.00               | 760.00 | 820.00 |
| $\Delta$                           | +1.88                | +2.69  | +2.13  |

The deviations are very small in this case, but they do not correspond in direction with the temperature and volume changes.

#### IV. Carbon Tetrachloride and Benzene.

A fresh quantity of carbon tetrachloride was obtained from Kahlbaum; it was distilled through the 18 column dephlegmator, and was found to boil quite constantly. It was distilled over phosphoric oxide.

The boiling point and sp. gr. of benzene have been already given. Those of carbon tetrachloride are as follows :

##### Boiling point.

| Pressure,<br>mm. | Temperature |                  |
|------------------|-------------|------------------|
|                  | obs.        | corr. to 760 mm. |
| 757.0            | 76.62°      | 76.75°           |

##### Sp. gr. at 0°/4°.

1.63257

Old result 1.63255\*

\* Trans., 1891, 59, 911.



*Change of volume on mixing.*

| Molecular composition |        | Sp. gr. at 0°/4°         | ...      | 1·28415                       |
|-----------------------|--------|--------------------------|----------|-------------------------------|
| Carbon tetrachloride  | 50·10  | Volume of a gram obs.... |          | 0·77873                       |
| Benzene .....         | 49·90  | " "                      | calc.... | 0·77991                       |
|                       | 100·00 |                          |          | Difference = - 0 00118        |
|                       |        |                          |          | Percentage difference - 0·151 |

From data obtained by Thorpe and Rodger (Trans., 1897, 71, 363) the percentage contraction would be 0·06, and observations of F. D. Brown (Trans., 1881, 39, 202) lead to the value 0·022.

*Change of temperature on mixing.*

| Molecular composition.     |          |        |          |         |
|----------------------------|----------|--------|----------|---------|
| Carbon tetrachloride ..... | 50·1     |        |          |         |
| Benzene .....              | 49·9     |        |          |         |
|                            | 100·0    |        |          |         |
| Carbon tetrachloride.      | Benzene. | Mean.  | Mixture. | Δ.      |
| Temp. ... 18·33°           | 18·29°   | 18·31° | 17·62°   | - 0·69° |

As is often the case with liquids which are not closely related, there is contraction associated with a fall in temperature on mixing :

*Boiling Points of Mixtures of Carbon Tetrachloride and Benzene.*

## Molecular percentages of benzene.

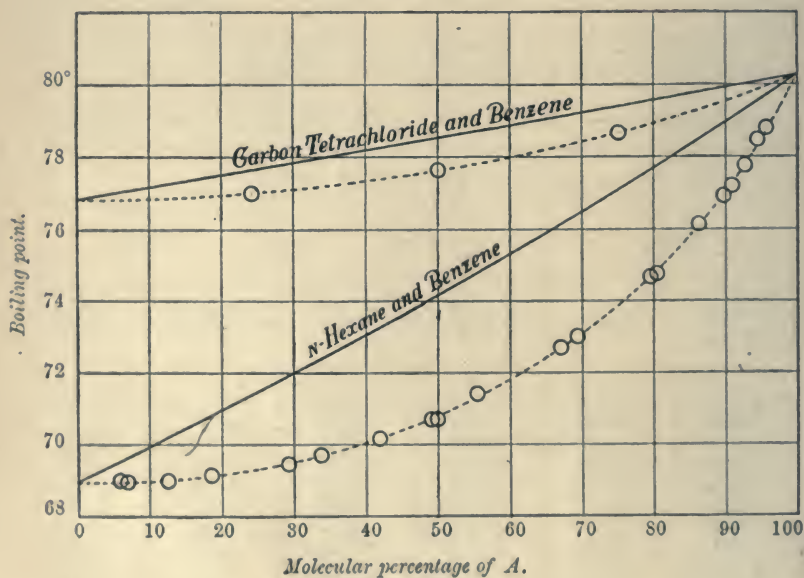
| 24·20.           |        | 50·00.           |        | 75·00.           |        |
|------------------|--------|------------------|--------|------------------|--------|
| Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  | Pressure,<br>mm. | Temp.  |
| 655·6            | 72·22° | 658·9            | 73·01° | 657·7            | 73·99° |
| 668·4            | 72·86  | 670·7            | 73·56  | 670·3            | 74·59  |
| 681·6            | 73·47  | 682·1            | 74·11  | 681·5            | 75·11  |
| 693·7            | 74·03  | 693·8            | 74·64  | 693·5            | 75·69  |
| 707·4            | 74·64  | 705·8            | 75·21  | 706·0            | 76·26  |
| 721·1            | 75·31  | 718·5            | 75·83  | 718·1            | 76·82  |
| 734·6            | 75·93  | 729·5            | 76·33  | 733·2            | 77·46  |
| 746·1            | 76·43  | 743·3            | 76·92  | 743·4            | 77·97  |
| 753·6            | 76·69  | 754·3            | 77·40  | 752·0            | 78·35  |
| 764·3            | 77·18  | 763·2            | 77·79  | 762·7            | 78·78  |
| 774·5            | 77·62  | 773·9            | 78·25  | 773·3            | 79·23  |
| 785·1            | 78·03  | 784·5            | 78·63  | 784·8            | 79·69  |
| 795·9            | 78·54  | 794·9            | 79·10  | 796·4            | 80·17  |
| 803·0            | 79·03  | 804·8            | 79·54  | 807·6            | 80·65  |
| 819·7            | 79·53  | 815·9            | 80·00  | 819·3            | 81·12  |
| 832·6            | 80·03  | 827·4            | 80·45  | 830·4            | 81·57  |
| 844·4            | 80·52  | 838·2            | 80·93  | 841·4            | 82·02  |
| —                | —      | 849·1            | 81·36  | —                | —      |

The boiling points at 700, 760, and 820 mm., read from the curve, are as follows:

| Pressure,<br>mm. | Molecular percentages of benzene. |       |       |
|------------------|-----------------------------------|-------|-------|
|                  | 24.20                             | 50.00 | 75.00 |
| 700              | 74.32                             | 74.95 | 75.98 |
| 760              | 77.00                             | 77.65 | 78.67 |
| 820              | 79.53                             | 80.17 | 81.15 |

The deviations of the observed boiling points from the theoretical curves are shown in Fig. 2. It will be seen that they are much larger than in the case of closely related liquids.

FIG. 2.



The constants for Biot's larger formula for carbon tetrachloride are given in a former paper (Trans., *loc. cit.*).

The comparison of pressures is given in the following table:

| Molecular percentage<br>of benzene. | Calculated pressures. |        |        |
|-------------------------------------|-----------------------|--------|--------|
| 24.20                               | 685.72                | 745.11 | 804.84 |
| 50.00                               | 680.13                | 739.85 | 799.02 |
| 75.00                               | 683.45                | 743.30 | 801.96 |
| Mean.....                           | 683.1                 | 742.7  | 801.9  |
| Observed pressures                  | 700.0                 | 760.0  | 820.0  |
| $\Delta$                            | -16.9                 | -17.3  | -18.1  |

The differences are much larger than with the pairs of closely related liquids and correspond in direction with the temperature change.

Reference has been made to the fact that mixtures of these substances have been investigated by Linebarger, Lehfeldt, and Zawidski. The method employed by Linebarger does not appear to give good results with volatile liquids, and his observed vapour pressures differ somewhat widely from those of Lehfeldt and of Zawidski.

A comparison of the results obtained by the latter experimenters with our own may be made by calculating the theoretical vapour pressures of the mixtures from the formula  $P = \frac{pP_A + (100 - p)P^a}{100}$ , and the ratios of the observed to the calculated pressures  $\frac{P'}{P}$ .

| Young and Fortey.                      |        |        |                  | Zawidski (at 49.99°). |        |       |                  |
|--|--------|--------|------------------|-----------------------|--------|-------|------------------|
| Molecular<br>percentage<br>of benzene. | $P'$ . | $P$ .  | $\frac{P'}{P}$ . | $p$ .                 | $P'$ . | $P$ . | $\frac{P'}{P}$ . |
| $p$ .                                  |        |        |                  |                       |        |       |                  |
| 24.20                                  | 700    | 685.72 | 1.021            | 23.48                 | 306.8  | 298.6 | 1.028            |
| "                                      | 760    | 745.11 | 1.020            | 32.45                 | 305.2  | 295.0 | 1.035            |
| "                                      | 820    | 804.84 | 1.019            | 44.13                 | 301.0  | 290.3 | 1.037            |
| 50.00                                  | 700    | 680.13 | 1.029            | 60.47                 | 294.5  | 283.8 | 1.038            |
| "                                      | 760    | 739.85 | 1.027            | 70.53                 | 288.3  | 279.8 | 1.030            |
| "                                      | 820    | 799.02 | 1.026            | 74.85                 | 285.4  | 278.1 | 1.026            |
| 75.00                                  | 700    | 683.45 | 1.024            | 82.42                 | 281.5  | 275.0 | 1.024            |
| "                                      | 760    | 743.30 | 1.022            | 88.30                 | 277.6  | 272.7 | 1.018            |
| "                                      | 820    | 801.96 | 1.022            | 94.93                 | 271.8  | 270.0 | 1.007            |



Lehfeldt (at 50°).

| $p$ . | $P'$ . | $P$ . | $\frac{P'}{P}$ . |
|-------|--------|-------|------------------|
| 38.69 | 302.3  | 295.0 | 1.025            |
| 69.56 | 290.0  | 282.9 | 1.025            |
| 84.22 | 231.0  | 277.1 | 1.014            |

At first sight, our results appear to agree better with Lehfeldt's but in our experiments the ratio  $\frac{P'}{P}$  increases as the pressure falls, and if the rate of increase remained constant, the ratios corresponding to the pressures at 50° would be very close to those derived from Zawidski's observations.

The boiling points of mixtures of *n*-hexane and benzene under normal pressure have been determined by Jackson and Young (*loc. cit.*). The curve showing the relation of temperature to composition is given in Fig. 2 (p. 62). The sp. grs. of these hydrocarbons are given in the above paper, and also the expansion on mixing in different proportions. For equal molecules, this would be 0.399 per cent. The temperature change has now been determined with the following results:

|       | <i>n</i> -Hexane. | Benzene. | Mean.  | Mixture. | $\Delta$ . |
|-------|-------------------|----------|--------|----------|------------|
| Temp. | 17.27°            | 17.23°   | 17.25° | 12.55°   | - 4.7°     |

Although the volume and temperature changes correspond in direction, the latter is relatively much the greater of the two.

## DISCUSSION OF RESULTS.

### *Experimental Errors.*

Owing to the fact that when a mixed liquid evaporates the composition of the vapour differs in general from that of the liquid in such a manner that the residual liquid becomes richer in the less volatile component, it is of great importance that in determining the boiling point the vapour phase should be kept as small as possible.

The greater the difference between the vapour pressures of the two components into which the mixture would separate on distillation (whether the original substances, or one of them and a mixture of constant boiling point), the greater, as a rule, the difference between the composition of the liquid and of the vapour.

In the actual experiments it was noticed that with mixtures of carbon tetrachloride and benzene the rate of ebullition could be considerably altered without appreciably affecting the reading of the

thermometer in the vapour, whereas with *n*-hexane and *n*-octane a difference of  $0.5^{\circ}$  was easily produced. For this reason, the experimental errors in the latter case are probably much larger, and to get thoroughly satisfactory results, inasmuch as the neck of the vessel could not be made much smaller, it would be necessary to use a much larger bulb so as to increase the volume of the liquid relatively to that of the vapour.

If a carefully dehydrated liquid is exposed to the air, even for a short time, especially if it is poured from one vessel to another so that a large surface is exposed to the air, a certain amount of moisture is almost invariably absorbed. It is not only liquids which are regarded as hygroscopic which thus absorb moisture, but even substances like benzene and the paraffins, which are classed as non-miscible with water. As a matter of fact, it is probable that no two liquids are absolutely non-miscible, and certainly all commonly occurring liquid organic compounds can dissolve appreciable amounts of water.

When such a liquid as benzene or carbon tetrachloride, containing a minute amount of dissolved water, is heated, a mixture of minimum boiling point will first be formed, and the first small portion of distillate will contain the whole, or at least the greater part, of the water, and will probably be turbid.

It is almost impossible to mix two liquids together in such a way as to avoid all absorption of water, and, as a matter of fact, it was noticed in every case that the liquid which condensed in the side-tube was at first slightly turbid. The condenser was allowed to become warm so that the vapour rose nearly to the top of the side-tube. The minute drops of condensed water adhered to the sides of the tube, and after cooling the condenser so as to cause the condensation again to take place at a lower level, the water was removed by means of a strip of filter paper. The process was repeated two or three times, if necessary, until no further turbidity could be seen. There was no appreciable loss of the mixture during the removal of the water.

#### *General Conclusions.*

1. The volume and temperature changes on mixing closely related substances are, in all the observed cases, very small, but it is only with chlorobenzene and bromobenzene that they can certainly be said to be within the limits of experimental error. With the two esters, these limits are very closely approached, whilst with benzene and toluene, which are somewhat less closely related, the changes are distinctly larger, and for mixtures of benzene with *n*-hexane and with carbon tetrachloride they are very much larger.

2. The formula  $P = \frac{pP_A + (100 - p)P_B}{100}$  is nearly, if not quite, true

for closely related liquids, even when the critical pressures are widely different; it is not generally true, however, for mixtures of liquids of normal molecular weight, such as benzene and *n*-hexane or benzene and carbon tetrachloride, which are not closely related, although Zawidski (*loc. cit.*) has shown that the formula does hold good for benzene and ethylene dichloride.

Of the five pairs of closely related liquids examined, it is only chlorobenzene and bromobenzene which show absolutely no temperature or volume change on mixing, and for mixtures of which the vapour pressures are accurately given by the above formula, and it is only this pair of liquids which have the same critical pressure. The deviations in the other cases are, however, so small that it remains an open question whether equality of critical pressure is a necessary criterion for absolute agreement with the formula. It appears at any rate that equality of critical pressure without closeness of chemical relationship is not a sufficient criterion.

It may certainly be stated that in the case of closely related substances, whatever their critical pressures, the deviations are, as a rule, at any rate, exceedingly small.

In the paper on "Fractional Distillation as a Method of Quantitative Analysis" (Trans., 1902, 81, 752), reasons were brought forward for concluding that *n*-hexane and benzene form a mixture of minimum boiling point, containing about 5 mols. per cent. of benzene, but the difference between the boiling points of this mixture and of *n*-hexane (about 0.035°) is too small to be measured by ordinary thermometric methods, and the existence of the mixture of constant boiling point has, indeed, not been actually proved by direct experiment. The maximum deviation of the observed from the theoretical boiling point curve is much greater than for carbon tetrachloride and benzene (3.4° against 0.9°), but at the same time the difference between the boiling points of the pure components is also much greater (11.3° against 3.4°). It seems, at first sight, improbable that two liquids such as benzene and carbon tetrachloride, which have so nearly the same value of  $\frac{dt}{dp} \cdot \frac{1}{T}$  at their boiling points (0.000121 and 0.000123) and for mixtures of which the maximum difference between the observed and the theoretical boiling points (0.9°) is so small, should form a mixture of minimum boiling point. Yet there are reasons for believing that such a mixture is formed and they may be stated shortly as follows:

Lehfeldt (*loc. cit.*) has determined the relations between the composition of the vapour and of the liquid for mixtures of these substances and gives the formula:

$$\log t = 0.065 + 0.917 \log \tau,$$



where  $t$  is the ratio of the mass of carbon tetrachloride to that of benzene in the vapour and  $q$  the ratio in the liquid.

Now, with these constants,  $\log t = \log q$  when  $q = 16.84$ , that is to say, a mixture containing 94.4 per cent. by weight, or 89.5 molecules per cent. of carbon tetrachloride, would distil unchanged.

Zawidzki (*loc. cit.*) has also determined the vapour pressures of mixtures of the same substances and the relations between the composition of vapour and of liquid, and he employs the formulæ

$$p_1 = P_1 x e^{\frac{a_1}{2}(1-x)^2 + \frac{a_2}{3}(1-x)^3} \quad \text{and} \quad p_2 = P_2 (1-x) e^{\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3},$$

where  $p_1$  and  $p_2$  are the partial pressures of the components (which are proportional to the number of their molecules in the vapour), and  $P_1$  and  $P_2$  the vapour pressures of the pure components at the temperature of observation;  $x$  is the molecular fractional amount of the first component;  $a_2$ ,  $a_3$ ,  $\beta_2$ , and  $\beta_3$  are constants, such that  $\beta_2 = a_2 + a_3$  and  $\beta_3 = -a_3$ . The constants given are  $a_2 = 0.308$ ;  $a_3 = 0.00733$ .

For  $x = 0.95$  ( $x$  representing the molecular fractional amount of carbon tetrachloride),  $p_1 = 292.71$ ,  $p_2 = 15.42$ , giving a total of 308.13, while the vapour pressure of pure carbon tetrachloride is 308.0. If these constants are correct, there is then a maximum vapour pressure, but it is so little higher than that of carbon tetrachloride that it would be hardly possible to observe it experimentally. It may, however, be

mentioned that Zawidzki gives the following values of  $\frac{d\pi}{dx}$  for

$x = 0$  and  $x = 1$  read from the vapour pressure curve;  $\left(\frac{d\pi}{dx}\right)_0 = +90$ ;

$\left(\frac{d\pi}{dx}\right)_1 = -4.3$ , so that he does assume the existence of a point of maximum pressure.

According to F. D. Brown (Trans., 1881, 39, 304), the relation between the composition of vapour and of liquid is given by the

formula  $\frac{x_1}{x_2} = c \frac{w_1}{w_2}$ , where  $x_1$  and  $x_2$  are the relative weights of the com-

ponents in the vapour and  $w_1$  and  $w_2$  in the liquid (or, of course,  $x$  and  $w$  may refer to the number of molecules if the molecular weights are normal). There is evidence, which will be given in a later publication, that Brown's law is true for mixtures the vapour pressures of

which are accurately given by the formula  $P = \frac{pP_A + (100-p)P_B}{100}$ , but

not otherwise. If, however, the pressure deviations are small, a

modification of the formula, namely,  $\frac{x_1}{x_2} = c' \frac{w_1}{w_2}$  (where  $c' = c_0 + ap$ ,  $c_0$  and  $a$  being constants), gives fairly good results.

For carbon tetrachloride and benzene, Lehfeldt's experimental results would lead to the formula  $\frac{x_B}{x_A} = (0.984 + 0.003p) \frac{W_B}{W_A}$ , whilst those of Zawidski are well represented by the formula

$$\frac{x_B}{x_A} = (0.961 + 0.0036p) \frac{W_B}{W_A}.$$

In the first case,  $c' = 1$  when  $p$  (the molecular percentage of benzene) = 6.7, and in the second case when  $p = 10.8$ ; and when  $c' = 1$  the mixture would distil without change of composition and at a constant temperature.

Lehfeldt's formula, as has already been shown, would indicate the existence of a mixture of constant boiling point containing 10.5 molecules per cent. of benzene.

All these considerations lead to the same conclusion, that a mixture of minimum boiling point is formed, but it is not possible to ascertain the composition of the mixture with any great accuracy.

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## VI.—*The Vapour Pressures and Boiling Points of Mixed Liquids. Part III.*

By SYDNEY YOUNG, D.Sc., F.R.S.

IN parts I and II (Trans., 1902, 81, 768; and this vol., p. 45) it has been shown that for two closely related chemical compounds, whether their critical pressures are equal or not, the vapour pressures of any mixture may be calculated with a close approximation to accuracy by the formula  $P = \frac{pP_A + (100 - p)P_B}{100}$ , when  $P$ ,  $P_A$ , and  $P_B$  are the vapour pressures of the mixture and of the two components  $A$  and  $B$  respectively at the same temperature, and  $p$  is the molecular percentage of  $A$ . In other words, the relation between the vapour pressures and the molecular composition of mixtures of the two liquids at constant temperature is represented, very nearly, at any rate, by a straight line.

On the other hand, the relation between the boiling points and the molecular composition of mixtures of two closely related compounds is represented by a curve which approximates more and more closely to a straight line as the difference,  $\Delta$ , between the boiling points of the two compounds under normal pressure diminishes. Thus, taking the

values calculated from the vapour pressures by means of the formula

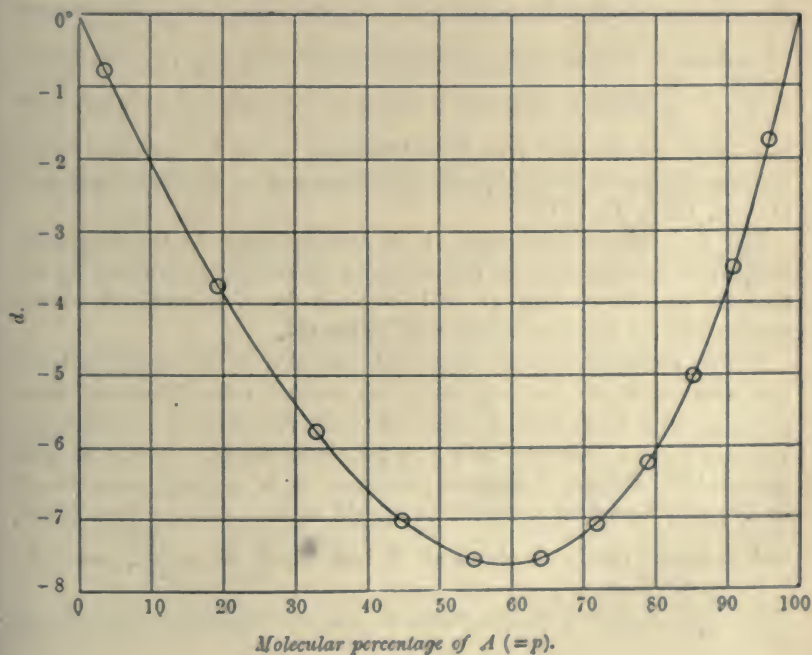
$$p = \frac{100(P_B - 760)}{P_B - P_A} \text{ as correct, we have the following results:}$$

TABLE I.

| Liquids in mixture. |                       | $\Delta$ . | Maximum deviation from straight line = $D$ . | Approximate molecular percentage of $A$ corresponding to $D = p_D$ . |
|---------------------|-----------------------|------------|--|--|
| $A$ .               | $B$ .                 |            |  |  |
| <i>n</i> -Octane    | <i>n</i> -Hexane..... | 58.63°     | -10.80°                                      | 61.0   |
| Toluene             | Benzene .....         | 33.33      | -3.22  | 56.0   |
| Ethylbenzene        | Toluene .....         | 25.57      | -2.22  | 54.5   |
| Bromobenzene        | Chlorobenzene         | 24.1       | -1.91  | 55.0   |
| Ethyl propionate    | Ethyl acetate         | 21.96      | -1.83  | 54.5   |

It is evident that, as  $\Delta$  diminishes,  $D$  falls rapidly and  $p_D$  slowly.

I have calculated values of  $p$  and the corresponding deviations,  $d$ , for a number of pairs of closely related liquids in order, if possible, to find the relation between  $\Delta$ ,  $D$ , and  $p_D$ . The data for one pair of liquids are given below, and the curve obtained by plotting  $d$  against  $p$  is shown in the figure. From the form of this curve it is evident that the





maximum deviation,  $D$ , can be ascertained with far greater accuracy than the corresponding molecular percentage,  $p_D$ , of  $A$ . The difficulty in estimating the true value of  $p_D$  increases as  $\Delta$  diminishes, and becomes very great when  $\Delta$  is less than  $2^\circ$  or  $3^\circ$ .

The two liquids are, A, propyl acetate, b. p.  $101.58^\circ$ , and B, methyl acetate, b. p.  $57.15^\circ$ ;  $\Delta = 44.43^\circ$ .

TABLE II.

| Temp.<br>= $t$ | Vapour Pressures. |           | $P_B - 760$ ,<br>mm. | $P_B - P_A$ ,<br>mm. | $p$ . | $t' =$<br>$57.15 + \frac{\Delta p}{100}$ | $d =$<br>$t - t'$ |
|----------------|-------------------|-----------|----------------------|----------------------|-------|--|-------------------|
|                | A.<br>mm.         | B.<br>mm. |                      |                      |       |  |                   |
| 58             | 158.7             | 782.9     | 22.9                 | 624.2                | 3.67  | 58.78°                                   | -0.78°            |
| 62             | 186.9             | 897.8     | 137.8                | 710.9                | 19.38 | 65.76                                    | -3.76             |
| 68             | 219.2             | 1025.6    | 265.6                | 806.4                | 32.94 | 71.78                                    | -5.78             |
| 70             | 256.1             | 1167.2    | 407.2                | 911.1                | 44.69 | 77.01                                    | -7.01             |
| 74             | 297.8             | 1323.8    | 563.8                | 1026.0               | 54.95 | 81.57                                    | -7.57             |
| 78             | 345.0             | 1496.3    | 736.3                | 1151.3               | 63.95 | 85.56                                    | -7.56             |
| 82             | 398.0             | 1685.9    | 925.9                | 1287.9               | 71.89 | 89.09                                    | -7.09             |
| 86             | 457.5             | 1893.5    | 1133.5               | 1436.0               | 78.94 | 92.22                                    | -6.22             |
| 90             | 523.9             | 2120.3    | 1360.3               | 1596.4               | 85.21 | 95.01                                    | -5.01             |
| 94             | 597.7             | 2367.5    | 1607.5               | 1769.8               | 90.83 | 97.51                                    | -3.51             |
| 98             | 679.5             | 2636.3    | 1876.3               | 1956.8               | 95.88 | 99.75                                    | -1.75             |

The data for 19 pairs of liquids are given in Table III (p. 71). The values of  $c\left(\frac{dt}{dp} \cdot \frac{1}{T} \text{ where } p = \text{pressure}\right)$ , which will be referred to later, have been taken for the most part from the paper on the "Correction of the Boiling Points of Pure Liquids from Observed to Normal Pressure" (Trans., 1902, 81, 777).

The molecular percentages of A corresponding to the maximum temperature deviations are reproduced with sufficient accuracy by the formula  $p_D = 50 + 0.18\Delta$ , as will be seen by a comparison of the numbers in the last two columns of Table III.

Of the various groups of compounds included in the table, the halogen derivatives of benzene show the closest resemblance in their physical properties, and it may be well to consider first the six possible pairs obtainable from the pure compounds. It will be seen from table IV that, for these mixtures,  $D$  is roughly proportional to  $\Delta^2$ ; but the actual temperature should also be taken into account, and a better result is obtained if, instead of  $K_1 = \frac{D}{\Delta^2}$ , we take

$K_2 = \frac{DT}{\Delta^2}$ , where  $T$  is the mean of the two boiling points on the

TABLE III.

| Liquids in mixture. |                | Boiling points (absolute).* |        | $\Delta$ . | $c \times 10^4$ . |     | $D$ .  | $r_D$       |                     |
|---------------------|----------------|-----------------------------|--------|------------|-------------------|-----|--------|-------------|---------------------|
| A.                  | B.             | A.                          | B.     |            | A.                | B.  |        | From curve. | $50 + 0.18\Delta$ . |
| Chlorobenzene       | Fluorobenzene  | 405.00                      | 353.20 | 46.80      | 120               | 120 | -7.60  | 58.5        | 58.5                |
| Bromobenzene        | "              | 429.00                      | 358.20 | 70.80      | "                 | "   | -16.60 | 63.0        | 62.8                |
| Iodobenzene         | "              | 461.45                      | 358.20 | 103.25     | "                 | "   | -32.80 | 68.5        | 68.5                |
| Bromobenzene        | Chlorobenzene  | 429.00                      | 405.00 | 24.10      | "                 | "   | -1.91  | 55.0        | 54.4                |
| Iodobenzene         | "              | 461.45                      | 405.00 | 56.45      | "                 | "   | -9.56  | 60.0        | 60.2                |
| Iodobenzene         | Bromobenzene   | 461.45                      | 429.00 | 32.35      | "                 | "   | -3.16  | 56.0        | 55.9                |
| n-Hexane            | n-Pentane      | 341.97                      | 309.13 | 32.84      | 122               | 125 | -4.04  | 55.0        | 55.9                |
| n-Heptane           | "              | 371.46                      | 309.13 | 62.33      | 121               | 125 | -13.84 | 61.5        | 61.2                |
| n-Octane            | "              | 398.60                      | 309.13 | 89.50      | 119               | 125 | -27.15 | 66.0        | 64.0                |
| n-Heptane           | n-Hexane       | 371.46                      | 341.97 | 29.49      | 121               | 122 | -3.08  | 55.0        | 55.3                |
| n-Octane            | "              | 398.60                      | 341.97 | 56.63      | 119               | 122 | -10.80 | 61.0        | 60.2                |
| n-Octane            | n-Heptane      | 398.60                      | 371.46 | 27.14      | 119               | 121 | -2.43  | 55.0        | 54.9                |
| Toluene             | Benzene        | 383.60                      | 353.27 | 30.33      | 120               | 121 | -8.22  | 56.0        | 55.5                |
| Ethylbenzene        | Toluene        | 409.17                      | 383.60 | 25.57      | 120               | 120 | -2.22  | 51.5        | 54.6                |
| Ethyl acetate       | Methyl acetate | 350.14                      | 330.20 | 19.95      | 114               | 113 | -1.62  | 55.0        | 53.6                |
| Propyl acetate      | "              | 374.58                      | 330.20 | 44.38      | 114               | 113 | -7.63  | 58.0        | 58.0                |
| Propyl acetate      | Ethyl acetate  | 374.58                      | 350.15 | 24.43      | 114               | 114 | -2.26  | 56.0        | 54.5                |
| Ethyl propionate    | "              | 372.12                      | 350.15 | 21.96      | 113               | 114 | -1.63  | 54.5        | 54.0                |
| Propyl alcohol      | Ethyl alcohol  | 370.47                      | 351.32 | 19.15      | 94                | 94  | -1.67  | 53.0        | 53.5                |

\* The boiling points have been calculated from Biot's formula and usually differ slightly from those directly observed.

absolute scale. The agreement is still better if we take into account the fact that the molecular percentage of  $A$  corresponding to  $D$

depends on  $\Delta$ , and if we write  $K_3 = \frac{DT'}{\Delta^2}$ , where

$$T' = \frac{(50 + 0.18\Delta)T_A + (50 - 0.18\Delta)T_B}{100}.$$

TABLE IV.

| Liquids in mixture. |               | $K_1 = \frac{D}{\Delta^2}$ | $K_2 = \frac{D \cdot T}{\Delta^2}$ | $K_3 = \frac{D \cdot T'}{\Delta^2}$ |
|---------------------|---------------|----------------------------|------------------------------------|-------------------------------------|
| A.                  | B.            |                            |                                    |                                     |
| Chlorobenzene       | Fluorobenzene | -0.00347                   | -1.324                             | -1.338                              |
| Bromobenzene        | "             | -0.00330                   | -1.200                             | -1.330                              |
| Iodobenzene         | "             | -0.00308                   | -1.261                             | -1.320                              |
| Bromobenzene        | Chlorobenzene | -0.00329                   | -1.371                             | -1.375                              |
| Iodobenzene         | "             | -0.00300                   | -1.300                             | -1.317                              |
| Iodobenzene         | Bromobenzene  | -0.00302                   | -1.344                             | -1.350                              |

The value of  $c$  is the same for the four halogen derivatives of benzene, and for a large number of compounds it varies only slightly, but it is considerably lower for substances the molecules of which are associated in the liquid state. Of the compounds included in table

III, *n*-pentane and *n*-hexane have the highest values of *c* (0.000125 and 0.000122) and ethyl alcohol and propyl alcohol the lowest (both 0.000094), and we may usefully compare mixtures of *n*-pentane and *n*-hexane with those of the two alcohols.

The values of  $K_3$  are  $-1.227$  and  $-1.643$  respectively, but if we multiply these numbers by the values of  $c'$  calculated, like those of  $T'$ , from the equation  $c' = \frac{(50 + 0.18\Delta)c_A + (50 - 0.18\Delta)c_B}{100}$ , we get for  $K_4 = \frac{D \cdot c' \cdot T'}{\Delta^2}$  the values  $-0.000151$  and  $-0.000154$ , which agree well together.

For any series of closely related compounds there is usually no great variation in the value of *c*, but as has been shown in the paper referred to (Trans., 1902, 81, 781) the tendency, in a homologous series, is for *c* to diminish as the molecular complexity increases. Thus for the normal paraffins, pentane, hexane, heptane, and octane, the values of *c* are 0.000125, 0.000122, 0.000121, and 0.000119 respectively. Calculating  $K_4$  for iodobenzene and fluorobenzene, which have the same value of *c*, 0.000120, and for octane and pentane with the values 0.000119 and 0.000125, we get  $-0.0001584$  and  $-0.0001510$  respectively. If now we multiply these values of  $K_4$  by  $\frac{c_B}{c_A}$  we get  $-0.0001584$  and  $-0.0001586$ , and generally, the best agreement is obtained with the formula

$$K_5 = \frac{D \cdot c' \cdot T' \cdot c_B}{\Delta^2 \cdot c_A}.$$

Taking  $-0.000158$  as the mean value  $K_5$  so that

$$D = -\frac{0.000158 \Delta^2 c_A}{c' \cdot T' \cdot c_B},$$

we get the results given in table V (p. 73).

Let us now consider the behaviour of liquids which are not closely related to each other. We must find, firstly, whether the maximum deviation,  $D_1$ , calculated from the vapour pressures of the components on the assumption that the formula  $P = \frac{pP_A + (100 - p)P_B}{100}$  holds good, agrees with those given by the equation  $D_2 = -\frac{0.000158 \Delta^2 c_A}{c' \cdot T' \cdot c_B}$ , and, secondly, whether the maximum deviations calculated from the vapour pressures agree with those directly observed.

We must also find whether the formula  $p_D = 50 + 0.18\Delta$  is applicable to mixtures of liquids which are not closely related.

The data for twenty pairs of liquids are given in Table VI (p. 74), the mixtures being arranged in ascending order of  $\frac{c_A}{c_B}$ .



TABLE V.

| Liquids in mixture. |                 | $D_1$<br>from<br>vap.<br>press. | $D_2$<br>from<br>formula. | $D_3$<br>observed. | Differences. |             |
|---------------------|-----------------|---------------------------------|---------------------------|--------------------|--------------|-------------|
| A.                  | B.              |                                 |                           |                    | $D_2 - D_1$  | $D_3 - D_1$ |
| Chlorobenzene       | Fluorobenzene   | -7.60                           | -7.48 <sup>c</sup>        | —                  | +0.12°       | —           |
| Bromobenzene        | "               | -16.60                          | -16.44                    | —                  | +0.16        | —           |
| Iodobenzene         | "               | -32.80                          | -32.73                    | —                  | +0.07        | —           |
| Bromobenzene        | Chlorobenzene   | -1.91                           | -1.83                     | -1.94              | +0.08        | -0.03       |
| Iodobenzene         | "               | -9.56                           | -9.56                     | —                  | 0            | —           |
| Iodobenzene         | Bromobenzene    | -3.16                           | -3.08                     | —                  | +0.08        | —           |
| n-Hexane            | n-Pentane.....  | -4.04                           | -4.12                     | —                  | -0.08        | —           |
| n-Heptane           | "               | -13.84                          | -13.97                    | —                  | -0.13        | —           |
| n-Octane            | "               | -27.15                          | -27.04                    | —                  | +0.11        | —           |
| n-Heptane           | n-Hexane .....  | -3.08                           | -3.13                     | —                  | 0.05         | —           |
| n-Octane            | "               | -10.80                          | -10.93                    | -10.53             | -0.13        | +0.27       |
| n-Octane            | n-Heptane ...   | -2.43                           | -2.48                     | —                  | -0.05        | —           |
| Toluene             | Benzene .....   | -3.22                           | -3.22                     | -3.06              | 0            | +0.16       |
| Ethylbenzene        | Toluene.....    | -2.22                           | -2.17                     | -1.99              | +0.05        | +0.23       |
| Ethyl acetate       | Methyl acetate  | -1.62                           | -1.64                     | —                  | -0.02        | —           |
| Propyl acetate      | "               | -7.63                           | -7.76                     | —                  | -0.13        | —           |
| Propyl acetate      | Ethyl acetate.. | -2.26                           | -2.28                     | —                  | -0.02        | —           |
| Ethyl propionate    | Ethyl acetate.. | -1.83                           | -1.84                     | -2.00              | -0.01        | -0.17       |
| Propyl alcohol      | Ethyl alcohol.  | -1.67                           | -1.71                     | —                  | -0.04        | —           |

The differences between the values of  $p_D$  calculated from the formula  $p_D = 50 + 0.18\Delta$  and those deduced from the vapour pressures are generally small when  $\frac{c_A}{c_B}$  does not differ greatly from unity; they are invariably positive when  $\frac{c_A}{c_B}$  is very small and negative when this ratio is large.

As regards the maximum deviations,  $D$ , it must be remembered that when  $\Delta$  has a low value, both  $D_1$  and  $D_2$ , and therefore  $D_2 - D_1$ , are necessarily very small; the relative as well as the actual differences should therefore be considered.

It will be noticed that when  $\frac{c_A}{c_B}$  is less than unity and  $\Delta$  is small,  $D_1$  may have a small positive value amounting, in the case of ethyl alcohol-*n*-hexane, to 0.23°. For values of  $\frac{c_A}{c_B}$  between 0.95 and 1.05 the actual differences,  $D_2 - D_1$ , are quite small, and in only one case in the whole table does the difference exceed 1°.

We may therefore conclude that the maximum temperature deviation which would be observed if the formula  $P = \frac{pP_A + (100 - p)P_B}{100}$

TABLE VI.

| Liquids in mixture.  |                      | Boiling points (abs.). |         | $\frac{c_A}{c_B}$ | $\Delta$ | $D_1$ from vap. press. | $D_2$ from formula. | $D_3$ obs. served.   | $D_2 - D_1$ | $D_3 - D_1$ | Mixture of constant boiling point.     |      | P.               |               |
|----------------------|----------------------|------------------------|---------|-------------------|----------|------------------------|---------------------|----------------------|-------------|-------------|--|------|------------------|---------------|
| A.                   | B.                   | A.                     | B.      |                   |          |                        |                     |                      |             |             | d.                                     | p.   | From vap. press. | From formula. |
| Propyl alcohol       | n-Pentane.....       | 370-47"                | 369-13" | 0.752             | 61.34°   | -11.66°                | -9.66°              | —                    | +2.00       | —           | ?                                      | ?    | 58               | 61            |
| Ethyl "              | Carbon tetrachloride | 351-32                 | 349-83  | 0.764             | 1.49     | +0.09                  | -0.01               | —                    | -0.10       | —           | Mixture formed                         | ?    | ?                | 50.3          |
| Ethyl "              | n-Hexane .....       | 351-32                 | 341-97  | 0.770             | 0.35     | +0.23                  | -0.29               | —                    | -0.52       | —           | -13.39                                 | 33.2 | 50               | 51.7          |
| Propyl "             | Benzene .....        | 370-47                 | 353-27  | 0.777             | 17.20    | -0.15                  | -0.94               | (-9.5)               | -0.79       | (-9.4)      | -6.4                                   | 20.9 | 34               | 53.1          |
| Water                | " .....              | 373-00                 | 353-27  | 0.818             | 19.73    | -0.58                  | -1.27               | —                    | -0.69       | —           | -16.85                                 | 29.6 | 47               | 53.6          |
| Benzene              | Carbon disulphide .. | 353-27                 | 319-25  | 0.958             | 34.02    | -4.02                  | -4.16               | -8.01                | -0.14       | -4.0        | —                                      | —    | 56.5             | 56.1          |
| Carbon tetrachloride | " ..                 | 349-83                 | 319-25  | 0.969             | 30.58    | -3.34                  | -3.41               | -5.82                | -0.07       | -2.5        | —                                      | —    | 56               | 55.5          |
| Benzene              | Carbon tetrachloride | 353-27                 | 349-83  | 0.984             | 3.44     | -0.02                  | -0.04               | -0.91                | -0.02       | -0.89       | { Mixture probably formed <sup>7</sup> | ?    | ?                | 50.6          |
| Benzene              | n-Hexane .....       | 353-27                 | 341-97  | 0.992             | 11.30    | -0.44                  | -0.47               | -3.88                | -0.03       | -3.44       | { Mixture probably formed <sup>8</sup> | ?    | 53               | 52.0          |
| Benzene              | Ether .....          | 353-27                 | 307-60  | 1.000             | 45.67    | -8.20                  | -8.06               | —                    | +0.14       | —           | —                                      | —    | 59               | 58.2          |
| Water                | Methyl alcohol ..    | 373-00                 | 337-89  | 1.000             | 35.11    | -5.57                  | -5.50               | -10.53               | +0.07       | -4.95       | —                                      | —    | 60               | 56.3          |
| Chloroform           | Acetone.....         | 334-2                  | 329-5   | 1.035             | 4.7      | —                      | -0.04               | —                    | —           | —           | +4.94                                  | 80   | —                | —             |
| Water                | Ethyl alcohol .....  | 373-00                 | 351-32  | 1.038             | 21.68    | -2.36                  | -2.21               | -12.26 <sup>5</sup>  | -0.15       | -5.9        | -2.46                                  | 10.6 | 58               | 53.9          |
| Water                | Propyl " .....       | 373-00                 | 370-47  | 1.038             | 2.33     | -0.06                  | -0.03               | (-11.4) <sup>4</sup> | +0.03       | (-11.3)     | -11.19                                 | 56.8 | 51               | 50.5          |
| Benzene              | Methyl " .....       | 353-27                 | 337-70  | 1.210             | 15.37    | -1.77                  | -1.21               | (-14.0)              | +0.56       | (-12.2)     | -12.37                                 | 38.6 | 59               | 52.8          |
| Toluene              | Water.....           | 383-60                 | 373-00  | 1.212             | 10.60    | -0.95                  | -0.52               | —                    | +0.43       | —           | -20.28                                 | 44.4 | 56               | 51.9          |
| Carbon tetrachloride | Methyl alcohol ..    | 349-83                 | 337-89  | 1.242             | 11.94    | -1.26                  | -0.73               | —                    | +0.53       | —           | -14.31                                 | 44.6 | 57               | 52.1          |
| n-Octane             | Ethyl " .....        | 398-60                 | 351-32  | 1.266             | 47.27    | -11.34                 | -10.85              | —                    | +0.49       | —           | —                                      | ?    | 64               | 58.5          |
| Toluene              | " ..                 | 383-60                 | 351-32  | 1.277             | 32.28    | -6.09                  | -5.24               | —                    | +0.85       | —           | Mixture formed                         | ?    | 62.5             | 55.8          |
| Benzene              | " ..                 | 353-27                 | 351-32  | 1.287             | 1.93     | -0.13                  | -0.02               | -11.26               | +0.11       | -11.1       | -11.16                                 | 55.2 | ?                | 50.3          |

1 F. D. Brown, Trans., 1879, 35, 547.

2 Konowaloff, Ann. Phys. Chem., 1881, [III], 14, 34.

3 Noyes and Warfel, J. Amer. Chem. Soc., 1901, 23, 403.

7 From the determinations of the relative composition of liquid and vapour at 50° by Leifeldt (Phil. Mag., 1898, [v], 46, 42) and by Zawidski (Zeit. physikal. Chem., 1900, 35, 129), it appears probable that there is a mixture of maximum vapour pressure containing roughly about 5-10 molecules per cent. of benzene. It is quite possible that there may be a mixture of minimum boiling point at atmospheric pressure, but the difference between the boiling points of this mixture and of carbon tetrachloride must be exceedingly small.

It is most probable that benzene and n-hexane form a mixture of minimum boiling point (Trans., 1902, 81, 766).

2 F. D. Brown, Trans., 1881, 39, 304.

4 Ryland, Amer. Chem. J., 1899, 22, 381.

6 Thayer, J. Physical Chem., 1898, 2, 382.

 $D_2 = -11.7$ ;  $D_3 - D_1 = -11.6$ .

held good may be calculated with considerable accuracy from the equation  $D = - \frac{0.000158 \cdot \Delta^2 \cdot c_A}{c \cdot T^2 \cdot c_B}$ , when  $\frac{c_A}{c_B}$  has a value between 0.95 and 1.05 and probably between 0.9 and 1.1, and, in the majority of cases, within 1° whatever the value of  $\frac{c_A}{c_B}$ .

It is only in a comparatively small number of cases that  $D_3$  can be accurately ascertained, experimental data being either insufficient or altogether wanting, but there is evidence that the true boiling points of mixtures of liquids which are not closely related are, as a rule, considerably lower than those calculated from the vapour pressures, although occasionally higher, and, of the 20 pairs of liquids in the table, certainly 11 and probably at least 2 others form mixtures of minimum boiling point, and one forms a mixture of maximum boiling point.

In the great majority of cases where the formation of mixtures of minimum boiling point has been observed, one of the two liquids is a hydroxyl compound—an alcohol, an acid, or water—and water also forms such mixtures with all the lower alcohols except methyl alcohol. It is well known that molecules of these liquids are more or less associated in the liquid state, and we may therefore conclude that mixtures of minimum boiling point are most readily formed, and that  $D_3 - D_1$  has the greatest negative value when one or both of the liquids exhibit molecular association.

It is probable that the molecules of acetone and also of the lower aliphatic esters are associated to a slight extent in the liquid state and, according to Ryland (*Amer. Chem. J.*, 1899, 22, 384) the following pairs of liquids form mixtures of minimum boiling point: (1) Carbon disulphide and acetone, (2) carbon disulphide and methyl acetate, (3) carbon disulphide and ethyl acetate, (4) acetone and methyl acetate (5) acetone and ethyl iodide, (6) ethyl iodide and ethyl acetate. Zawidski (*Zeit. physikal. Chem.*, 1900, 35, 128) has also shown that the first and last of these pairs of liquids form mixtures of maximum vapour pressure.

According to Speyers (*Amer. J. Sci.*, 1900, [iv], 9, 341), a mixture of minimum boiling point cannot be formed when both constituents have normal molecular weights at all concentrations, but this conclusion does not appear to be borne out by the facts, and it is clear that when  $\Delta$  is very small, a comparatively slight difference between  $D_3$  and  $D_1$  would be sufficient to give rise to the formation of a mixture of minimum boiling point. It is probable that benzene and *n*-hexane, for which  $\Delta = 11.3^\circ$ , and carbon tetrachloride and benzene ( $\Delta = 3.44^\circ$ ), form such mixtures, and Ryland (*loc. cit.*) states that a mixture of carbon disulphide and ethyl bromide (boiling points  $45.5$ — $45.7^\circ$  and



37.5—38.5°;  $\Delta$  = about 7.6°), containing 32 per cent. by weight of carbon disulphide, boils 0.5° lower than ethyl bromide. Again Zawidski (*loc. cit.*) finds that methylal and carbon disulphide ( $\Delta$  = 4°) form a mixture of maximum vapour pressure.

The occurrence of mixtures of maximum boiling point or minimum vapour pressure is comparatively rare; in most of the known cases, one of the substances is an acid and the other a base or a compound of basic character: formic, acetic, or propionic acid with pyridine (Zawidski); hydrochloric acid and methyl ether (Friedel, *Bull. Soc. chim.*, 1875, [ii], 24, 160, 241); or the liquids are water and an acid: formic, hydrochloric, hydrobromic, hydriodic, hydrofluoric, nitric, or perchloric acid (Roscoe, this Journal, 1861, 13, 146; 1862, 15, 270; *Proc. Roy. Soc.*, 1862, 11, 493); but Ryland finds that such mixtures are also formed by chloroform and acetone ( $\Delta$  = 4.5°), and by chloroform and methyl acetate ( $\Delta$  = 4.5°), and the first observation has been confirmed by Zawidski and by Kuenen (*Phil. Mag.*, 1902, [vi], 4, 116).

In previous papers (Trans., 1902, 81, 708), attention has been drawn to the fact that the monohydric aliphatic alcohols may be regarded, on the one hand, as alkyl derivatives of water and, on the other, as hydroxyl derivatives of the paraffins and that, as the complexity of the alkyl group increases, the properties of the alcohols recede from those of water and approach those of a paraffin such as *n*-hexane or of benzene.

This point is well illustrated by the values of  $D_2 - D_1$  (or  $D_3 - D_2$  where  $D_1$  cannot be calculated). Except in the case of mixtures of ethyl alcohol with water and with benzene, the experimental data are not sufficiently complete to allow of accurate values of  $D_3$  being ascertained, and most of the results given in Table VII can only be regarded as approximate:

TABLE VII.

| Liquids in mixture. |                                | $D_1$ . | $D_2$ . | $D_3$ . | $\frac{D_3 - D_1}{D_3 - D_2}$ or |
|---------------------|--------------------------------|---------|---------|---------|----------------------------------|
| Water and           | Methyl alcohol .....           | -5.57°  | —       | -10.5°  | -4.9°                            |
| "                   | Ethyl alcohol .....            | -2.36   | —       | -12.26  | -9.9                             |
| "                   | <i>n</i> -Propyl alcohol ..... | -0.06   | —       | -11.4   | -11.3                            |
| "                   | Isobutyl alcohol .....         | —       | -0.2°   | -13.5   | -13.3                            |
| Benzene and         | Methyl alcohol .....           | -1.77   | —       | -14.0   | -12.2                            |
| "                   | Ethyl alcohol .....            | -0.13   | —       | -11.2   | -11.1                            |
| "                   | <i>n</i> -Propyl alcohol ..... | -0.15   | —       | -9.5    | -9.4                             |

[For water and benzene  $d$  = -16.85° for  $p$  = 29.6 and  $D_3 - D_1$  is probably not far from -30°.]

As regards mixtures of the alcohols with water, the negative value of  $D_2 - D_1$  increases, and with benzene it decreases as the complexity of the alkyl group becomes greater; or, in both cases, the closer the relationship between the components of the mixture the smaller is the difference between  $D_2$  and  $D_1$ .

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## VII.—*Note on Mixtures of Constant Boiling Point.*

By SYDNEY YOUNG, D.Sc., F.R.S.

In the year 1879, Thorpe (Trans., 35, 544) made the observation that when a mixture of equal volumes of carbon tetrachloride and methyl alcohol was distilled, 46·5 per cent. of the whole boiled constantly between 55·6° and 55·9°, that is, nearly 10° lower than the boiling point of the more volatile component.

From the vapour density of the mixture of constant boiling point, 41·82, Thorpe found its percentage composition to be :

|                           |       |
|---------------------------|-------|
| Carbon tetrachloride..... | 78·1  |
| Methyl alcohol .....      | 21·9  |
|                           | <hr/> |
|                           | 100·0 |

As the composition of such a mixture can, as a rule, be ascertained by distilling one of different but known composition through an efficient still-head and weighing the distillate that comes over below the middle temperature (Trans., 1902, 81, 752), it was suggested by Dr. Thorpe that I should determine the composition of this mixture of constant boiling point by the distillation method in order to compare the result with that calculated from the vapour density.

The carbon tetrachloride and the methyl alcohol used for the purpose were obtained from Kahlbaum, and in both cases a single distillation through an 18-column Young and Thomas dephlegmator was sufficient to give material of perfectly constant boiling point.

The boiling points observed by Thorpe and myself are given below :

|                            | Thorpe. | Young. |
|----------------------------|---------|--------|
| Carbon tetrachloride ..... | 76·6°   | 76·75° |
| Methyl alcohol .....       | 65·2    | 64·7   |

It has been shown (Trans., 1902, 81, 718) that methyl alcohol can best be obtained free from water by distillation through an efficient

still-head, and the fact that Thorpe's specimen boiled  $0.5^{\circ}$  higher than mine may indicate that his alcohol was not completely dehydrated.

Two mixtures containing excess of carbon tetrachloride and one with excess of methyl alcohol were distilled through a 5-column "evaporator" still-head and an additional observation of the boiling point was made. The results obtained are as follows:

*Boiling Points.*

|  | Pressure,<br>mm. | Temperature.    |                  |
|--|------------------|-----------------|------------------|
|  |                  | observed        | corr. to 760 mm. |
| I. $\text{CCl}_4$ in excess... ..        | 757.5            | $55.60^{\circ}$ | $55.70^{\circ}$  |
| II. " " " .....                          | 760.0            | $55.70$         | $55.70$          |
| III. $\text{CH}_3\cdot\text{OH}$ " ..... | 756.4            | $55.58$         | $55.72$          |
| IV. " " " .....                          | 757.9            | $55.61$         | $55.69$          |

Mean  $55.70$

This agrees very well with Thorpe's value,  $55.6$ — $55.9^{\circ}$ .

*Composition.*

|      | Weights taken.   |                               | Middle point.  | Weight below middle point. |            | Composition of mixture of constant boiling point. |                               |
|------|------------------|-------------------------------|----------------|----------------------------|------------|---|-------------------------------|
|      | $\text{CCl}_4$ . | $\text{CH}_3\cdot\text{OH}$ . |                | Observed.                  | Corrected. | $\text{CCl}_4$ .                                  | $\text{CH}_3\cdot\text{OH}$ . |
| I.   | 118.45           | 23.37                         | $66.2^{\circ}$ | 112.83                     | 113.18     | 79.35   | 20.65                         |
| II.  | 110.50           | 22.11                         | "              | 106.74                     | 107.09     | 79.35   | 20.65                         |
| III. | 81.75            | 41.00                         | $60.2$         | 101.85                     | 102.20     | 79.99   | 20.01                         |

In the second distillation, the loss was estimated by weighing both the distillate and the residue. The difference between the sum of these weights and that of the mixture taken was 0.36 gram, and, as there was not more than a single drop of liquid left in the still-head after cooling, the loss by evaporation was taken to be 0.35 gram in this and also the other two distillations. It will be seen that the two results obtained by distilling mixtures containing excess of carbon tetrachloride agree perfectly together, but that the percentage of methyl alcohol calculated from the weight of distillate from the mixture containing excess of that substance is 0.64 lower. The percentage of methyl alcohol found by Thorpe is 1.25 higher than the highest value found by the distillation method.

In order to find which value is the most correct, the distillates from I and II were mixed together and redistilled, and the specific gravity



of the distillate, which came over at a perfectly constant temperature, was determined at  $0^{\circ}/4^{\circ}$ , and was found to be 1.35280. A mixture of about the right composition was then made up and its specific gravity at  $0^{\circ}/4^{\circ}$  was determined:

| Weights taken.                  |               | Percentage composition. | Sp. gr. at $0^{\circ}/4^{\circ}$ . |
|---------------------------------|---------------|-------------------------|------------------------------------|
| $\text{CCl}_4$ .....            | 26.6315       | 79.40                   | 1.35236                            |
| $\text{CH}_3\cdot\text{OH}$ ... | 6.9100        | 20.60                   |                                    |
|                                 | <hr/> 33.5415 | <hr/> 100.00            |                                    |

If there were no change of volume on mixing the two liquids together, the specific gravity would be 1.34992; conversely, if the volume of the mixture obtained by distillation had been equal to the sum of the volumes of its constituents, its specific gravity would have been  $\frac{1.35280 \times 1.34992}{1.35236} = 1.35037$ , and the percentage composition of a mixture of this specific gravity would be:

|                           |              |
|---------------------------|--------------|
| Carbon tetrachloride..... | 79.44        |
| Methyl alcohol .....      | 20.56        |
|                           | <hr/> 100.00 |

We have thus the following data for the composition of the mixture of constant boiling point:

*Distillation Method.*

|                             | Thorpe.     | From excess of<br>$\text{CH}_3\cdot\text{OH}$ . | From excess of<br>$\text{CCl}_4$ . | From sp. gr. of<br>distillate and<br>made mixture. |
|-----------------------------|-------------|---|------------------------------------|--|
| $\text{CCl}_4$ .....        | 78.1        | 79.99   | 79.35                              | 79.44  |
| $\text{CH}_3\cdot\text{OH}$ | 21.9        | 20.01   | 20.65                              | 20.56  |
|                             | <hr/> 100.0 | <hr/> 100.00                                    | <hr/> 100.00                       | <hr/> 100.00                                       |

The last result, which agrees very well with that obtained by the distillation method when carbon tetrachloride was in excess in the original mixture, may probably be taken as the most correct.

The rather high percentage of methyl alcohol found by Thorpe may perhaps be partly accounted for by the presence of a trace of water, which would lower the vapour density of the mixture, but the chief cause of the error is, I believe, the difficulty of the separation of the mixture of constant boiling point from methyl alcohol, taken in conjunction with the fact that an ordinary distillation bulb was (presumably) used.

The following observations seem to confirm this view: When a pure liquid is distilled through a five-column "evaporator" still-head,

the drops which fall from the little funnels on the inverted tubes wet the glass at once and the liquid spreads itself in an even layer over the surface, unless the quantity of liquid in the flask is very small, when the vapour becomes considerably superheated and spheroidal drops may generally be seen in the lowest section, but not in the others. If, however, separation of the components of a mixture is taking place in the still-head, this is indicated by the formation of spheroidal drops.

In the distillation of mixtures of carbon tetrachloride and methyl alcohol, with the latter in excess, although the temperature of the vapour at the top of the still-head showed no rise until rather more than half the total quantity of liquid had come over, yet spheroidal drops were visible in the lowest section even at the beginning of the distillation, and they appeared in the second and third sections before the temperature showed any alteration. From this it appears that the vapour in the lowest section must have contained some excess of methyl alcohol during even the earliest stages of the distillation, and with an ordinary still-head this would be carried over and the percentage of methyl alcohol in the distillate would consequently be too high. It might, perhaps, be supposed that the temperature of the vapour would be appreciably raised by the presence of a small excess of methyl alcohol, but that this is not the case is proved by the fact that striæ, due to the great difference between the densities of methyl alcohol and of the mixtures of minimum boiling point, were clearly visible in the distillate as each drop fell, before the boiling point showed any sensible rise, and that they were very marked indeed when the temperature had risen  $0.2^{\circ}$ .

Thorpe states that the distillate, the vapour density of which was determined, boiled constantly between  $55.6^{\circ}$  and  $55.9^{\circ}$ , and I think that this small rise of  $0.3^{\circ}$  would be quite sufficient to account for the presence of a very appreciable excess of methyl alcohol, and if, as is almost certain, the separation was not quite perfect even at first, the 1.34 per cent. excess of alcohol is completely accounted for.

When mixtures containing excess of carbon tetrachloride were distilled through the 5-column "evaporator" still-head, no spheroidal drops were seen, even in the lowest section, until more than two-thirds of the total quantity had come over. It may therefore be concluded that the separation of the mixture of minimum boiling point from carbon tetrachloride is much easier than from methyl alcohol, and the following observations bear out this conclusion. (1) The spheroidal drops became very marked in the bottom section before they appeared at all in the second; (2) at a later stage, when the spheroidal drops had become very distinct in the third section, they had almost disappeared again in the lowest; (3) they had ceased to be visible in the

lowest section before the thermometer showed a marked rise, proving that at this stage the vapour in the tube above the top section consisted of the nearly pure mixture of constant boiling point, while that in the lowest section was nearly pure carbon tetrachloride; (4) the rise of temperature, when it at last took place, was exceedingly rapid, amounting, near the middle point, to about two degrees between two consecutive drops of distillate. It may be mentioned that in the distillations with carbon tetrachloride in excess, striæ were visible in the distillate before the thermometer indicated any perceptible rise of temperature. Of course the great difference between the density of the mixture of constant boiling point and that of either methyl alcohol or carbon tetrachloride makes the striæ in the distillate more easily visible than in the majority of cases, but the formation of these striæ in the distillate and, to an even greater extent, of the spheroidal drops in the still-head, generally affords useful indications of the progress of a distillation.

It is certain that if Thorpe's first distillate, coming over between 55.6 and 55.9°, had been redistilled, or if the original mixture had contained excess of carbon tetrachloride, the boiling point would have been almost perfectly constant for a considerable time, and the percentage of methyl alcohol in the distillate would have been lower.

It has been stated that a mixture containing 20.60 per cent. of methyl alcohol has the specific gravity 1.35236 at 0°/4°, whereas if there were no change of volume on mixing the constituents, the specific gravity would be 1.34992. The corresponding volumes of a gram are 0.73945 and 0.74078, and there is therefore a contraction of 0.00133 c.c. or 0.18 per cent. On the other hand, on mixing together 27.5 grams of carbon tetrachloride and 7.15 grams of methyl alcohol, there was a fall in temperature of 0.95°, so that when the two liquids are mixed together in the proportion required to form the mixture of constant boiling point, there is slight contraction accompanied by a distinct fall of temperature. This mixture, in fact, resembles that of *n*-propyl alcohol and water in many respects, as will be seen from the table below:

| Molecular composition of mixture .....                                | CCl <sub>4</sub> and CH <sub>3</sub> ·OH. |                     | C <sub>3</sub> H <sub>7</sub> ·OH and H <sub>2</sub> O. |                  |
|---|---|---------------------|---|------------------|
|   | CCl <sub>4</sub>                          | CH <sub>3</sub> ·OH | C <sub>3</sub> H <sub>7</sub> ·OH                       | H <sub>2</sub> O |
|   | 44.59                                     | 55.41               | 43.17   | 56.83            |
|   | 100.00                                    |                     | 100.00  |                  |
| Difference of boiling point from that of more volatile component..... | - 9.00°                                   |                     | - 9.47°   |                  |
| Percentage contraction on mixing in the right proportion .....        | 0.18                                      |                     | 1.9   |                  |
| Fall of temperature.....  | 0.95                                      |                     | about 1.2   |                  |



*Appendix.*

In the papers by Miss Fortey and myself on the properties of mixtures of the lower alcohols with water, with benzene, and with benzene and water (Trans., 1902, 81, 717), reference should have been made to papers by E. F. Thayer (*J. Physical Chem.*, 1898, 2, 382) and G. Ryland (*Amer. Chem. J.*, 1899, 22, 384). Thayer determined the boiling point, and, by means of Pulfrich's refractometer, the composition of the mixture of minimum boiling point which ethyl alcohol forms with benzene. The materials employed were not quite pure; the benzene, after agitation with sulphuric acid, was distilled through a Hempel's still-head, and showed a rise of  $0.5^{\circ}$  during the complete distillation, but the first and last 25 per cent. were rejected. The alcohol (95 per cent.) was dried with lime and copper sulphate and showed a rise of  $0.3^{\circ}$  during distillation through the same still-head, the first and last portions being again rejected.

Ryland gives a list of mixtures of constant boiling point which had previously been observed, and records the formation of more than 40 additional ones. In the case of methyl alcohol and benzene, and of ethyl alcohol and benzene, he shows that the percentage of alcohol in the mixture of minimum boiling point diminishes considerably as the pressure is reduced. The composition of the mixtures of benzene with these alcohols was determined by adding water and measuring the volume of benzene set free. The materials employed by Ryland do not appear to have been quite pure, for he gives a range of  $0.5^{\circ}$  for the boiling points of each of the three liquids.

Carveth (*J. Physical Chem.*, 1902, 6, 248) has also determined the boiling point of the mixture of ethyl alcohol and benzene by passing the vapour of alcohol into benzene, and of benzene into alcohol, and observing in each case the lowest temperature reached. He made experiments with absolute alcohol and commercial benzene, and also with the purest materials available.

The results obtained by Thayer, Ryland, Carveth, and by Young and Fortey are given below:

*Boiling Points reduced to 760 mm.*

|                            | Thayer. | Ryland.    | Carveth. | Young<br>and<br>Fortey. |
|----------------------------|---------|------------|----------|-------------------------|
| Ethyl alcohol .....        | —       | 77.5—78.0° | —        | 78.30°                  |
| Benzene.....               | 79.5°   | 79.0—79.5  | —        | 80.20                   |
| Ethyl alcohol and benzene  | 67.6    | 67—68      | 67.6°*   | 68.24                   |
| Methyl alcohol.....        | —       | 64.5—65    | —        | 64.70                   |
| Methyl alcohol and benzene | —       | 57.5—58    | —        | 58.34                   |

\* With absolute alcohol and commercial benzene,  $68.15^{\circ}$  and  $68.3^{\circ}$ .

*Percentages of Alcohol in Mixture of Constant Boiling Point.*

|                            | Thayer. | Ryland.   | Carveth. | Young<br>and<br>Fortey. |
|----------------------------|---------|-----------|----------|-------------------------|
| Ethyl alcohol and benzene  | 33.5    | 31.4—32.3 | —        | 31.76                   |
| Methyl alcohol and benzene | —       | 38.4—39.0 | —        | 39.55                   |

The boiling points observed by Thayer, Ryland, and Carveth are, in nearly every case, lower than those found by Miss Fortey and myself. We found that the boiling point of the mixture of ethyl alcohol and benzene was noticeably depressed by even traces of water, and it was only when the alcohol was completely dehydrated that the temperature  $68.24^{\circ}$  was observed.

Ryland states that methyl, ethyl, isopropyl, and amyl alcohols can be separated from toluene by distillation, but that *n*-propyl alcohol and isobutyl alcohol form with it mixtures of minimum boiling point. It has, however, been found by Miss Fortey and myself that ethyl alcohol and toluene do form such a mixture boiling at  $76.7^{\circ}$ , and that a ternary mixture of ethyl alcohol, toluene, and water is formed, with the boiling point  $74.55^{\circ}$ . As isopropyl alcohol resembles ethyl alcohol so closely in its properties, it seems almost certain that this alcohol would also form binary and ternary mixtures of constant boiling point with toluene and with toluene and water respectively.

Ryland also states that isobutyl alcohol and benzene can be separated by distillation, but this statement does not agree with our observation (Trans., 1902, 81, 748) that a mixture of minimum boiling point is formed. In this case, however, the boiling point,  $79.93^{\circ}$ , is very close to that of benzene,  $80.2^{\circ}$ , and the mixture contains only 9.3 per cent. of the alcohol. It is obviously impossible that very much time could have been devoted by Ryland to the purification of the large number of liquids he investigated, and as the mixtures were distilled only once with a plain still-head, it is not to be wondered at that the existence of the isobutyl alcohol-benzene mixture of constant boiling point should have escaped his notice.

To obtain trustworthy results, especially in the more difficult cases, it is necessary that the materials employed should be very carefully purified, and that an efficient still-head should be used.

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# VIII.—*The Action of Metallic Thiocyanates on Carbonyl Chloride.*

By AUGUSTUS EDWARD DIXON, M.D.

DURING the course of a series of experiments on the interaction between acid chlorides and metallic thiocyanates, it was observed that if carbonyl chloride dissolved in toluene be allowed to stand in contact with lead thiocyanate, a solution is presently obtained, which gives with alkaline lead and silver salts the desulphurisation reactions characteristic of a thiocarbimide or one of its immediate derivatives (Trans., 1899, 75, 389).

The object in view was to effect, if possible, the synthesis of the hitherto unknown carbonyldithiocarbimide,  $\text{CO}(\text{NCS})_2$ , thus :



and in the hope of attaining this end, an investigation was commenced, of which a short account is now offered to the Society.

Summarising the experimental outcome of this study, it may be stated that carbonyldithiocarbimide has been obtained in solution, but hitherto the writer has not succeeded in isolating it; the compound, like most of its congeners of the acidic class, exhibits some of the characters of a thiocyanate, but, under certain conditions, behaves exclusively as a thiocarbimide.\* Thus, for instance, it unites spontaneously with 1 mol. of alcohol, yielding a hemithiourethane,  $\text{NCS}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$  or  $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ , which is hydrolysed by boiling water with formation of thiocyanic acid; in like manner, if treated with a limited quantity of an aromatic base, such as aniline, it yields an additive compound,  $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ , decomposable by hot water into thiocyanic acid, carbon dioxide, and phenylthiourea. On the other hand, if allowed to stand in contact with excess of aniline, it combines with 2 mols. of the latter, thereby producing the dithiocarbamide,  $\text{CO}(\text{NH}\cdot\text{CS}\cdot\text{NHPh})_2$ .

From the result with alcohol just mentioned, it was anticipated that carbonyl chloride would interact with alcoholic solution of potassium or barium thiocyanate, so as to yield the above hemithiourethane; but it was found that the chloride first attacks the alcohol, producing ethyl chlorocarbonate; this, in turn, forms carboxyethylthiocarbimide,  $\text{CO}_2\text{Et}\cdot\text{NCS}$ , which, uniting with more alcohol, is converted into diethylimidodithiocarbonate,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ .

\* Describing it as "a form of tautomerism," the author has lately called attention to the occurrence of this phenomenon amongst the "thiocyanates" of electro-negative radicles (Trans., 1901, 79, 541).



Notwithstanding that many experiments have been carried out, the work now extending over some years, it has not even yet been found practicable to devise really satisfactory conditions for the primary interaction, but as it could serve no useful purpose to submit a detailed account of all the various methods tried and their results, a mere outline is here given, sufficient to indicate the main lines on which the problem has been attacked.

#### EXPERIMENTAL.

Preliminary qualitative experiments were very encouraging; the cold solution of carbonyl chloride in toluene, when mixed with excess of lead thiocyanate, gave a marked reaction for thiocarbimide within even a few hours if boiled with alkaline lead tartrate; whilst after some days a very copious desulphurisation was noticeable. If brought into contact with carefully dried potassium thiocyanate, a well-marked blackening could thus be got within 10 minutes, the amount of desulphurising product increasing quickly on standing. But although the interaction commences readily enough, it soon appeared, from larger quantitative experiments, that it is incomplete: even when three or four times the theoretical amount of metallic thiocyanate was used and the time of keeping extended to as much as 4 months, shaking at frequent intervals, the greater part of the phosgene still remained undecomposed. Minute subdivision of the salt, or the addition of it in repeated fresh charges, appeared to have no considerable influence on the result; in one case, the mixture, placed in a globular flask containing rounded garnets and lying nearly horizontal, was rotated by means of a turbine for a week, the idea being to remove mechanically the metallic chloride from the surface of the solid thiocyanate; but this also failed to bring about anything like complete interaction.

Heating under pressure in a sealed vessel was tried at temperatures varying from  $60^{\circ}$  to  $150^{\circ}$ ; this was found to accelerate the process, although at high temperatures a good deal of collateral decomposition takes place, but, so far, every attempt to complete it has failed. Naturally, the thiocyanates were varied also, those of mercury, lead, barium, sodium, and potassium being tried; all interacted more or less readily, but the first-named was found to produce troublesome quantities of an amorphous, metallic derivative, somewhat soluble in toluene and other solvents, and consequently its use was discontinued.

No attempts were made in these earlier experiments to analyse quantitatively the products; in all cases, the toluene solution was filtered off by means of the pump from the metallic residue; usually, it was heated for some hours in an open vessel on the water-bath in

order to expel unchanged carbonyl chloride; sometimes the greater part of the solvents (toluene and the benzene used in washing) was distilled off under diminished pressure; the solution or residue of distillation was then mixed with a base or an alcohol in order to obtain the corresponding additive compound if a thiocarbimide should be present.

By distilling under diminished pressure, it was hoped that the phosgene would first come off, and next the thiocarbimide, should the latter volatilise without decomposition; otherwise that the solvents might be removed, leaving a residue consisting entirely or in part of thiocarbimide. In practice, however, it appeared, first, that the whole of the carbonyl chloride is by no means easily withdrawn from its solution in toluene, and secondly, that a large proportion of the thiocarbimide is carried over along with the solvents; so that, in the end, little thiocarbimide product is left, whilst the distillates consist in great part of the latter, together with the solvents and unchanged phosgene. But although it was not found practicable to isolate the thiocarbimide in this way, some indication of its presence was obtained, for it was noticed that if the distillation be continued until the phosgene is almost completely eliminated, the residue has now a sharp, tear-exciting odour, closely resembling, but fainter than, that of acetylthiocarbimide; this odour cannot be perceived, or at all events distinguished, in presence of any considerable quantity of the strongly smelling organic chloride.

After numerous experiments, the method of operating eventually adopted was to heat about 100 c.c. of phosgene in toluene (20 per cent. of  $\text{COCl}_2$ ), with at least double the calculated amount of dried and sifted potassium, or better sodium, thiocyanate, in an autoclave at  $100^\circ$  for six hours at a time. After cooling, the autoclave was opened, the mixture well ground up by means of a strong glass rod, and the process repeated (occasionally adding small fresh charges of thiocyanate), until the total duration of heating amounted to 30 hours. At each time of opening, some acid gas escaped (50 to 100 c.c.), smelling of carbonyl chloride, and causing a turbidity with lime-water. If led into silver nitrate solution, it gave a white precipitate of silver chloride: when passed through faintly acid solutions of lead, copper, or cadmium salts, they remained clear, but with alkaline solutions, precipitates of the corresponding sulphides were obtained. Presumably, therefore, the gas contained carbonyl sulphide, and traces of carbonyl chloride, together with some hydrogen chloride, the last being produced by interaction of the carbonyl chloride with the traces of moisture absorbed by the alkali thiocyanate, and the sulphide through the decomposition of this salt by the mineral acid:



If dry lead thiocyanate be used, little or no gas is produced.



By means of the filter pump, the reaction product was separated into (1) a brownish solid residue, and (2) a clear, reddish-yellow filtrate: from the residue cold water extracted chloride and thiocyanate, leaving an amorphous brown powder, which gave the reactions for  $\phi$ -sulphocyanogen, and contained a little iso-persulphocyanic acid: the filtrate was abundantly desulphurised by heating with alkaline salts of mercury, lead, and silver, and when shaken up with cold water, gave a distinct, but not intense, red coloration on the addition of ferric chloride. This solution still contained much unaltered carbonyl chloride, most of which was removed by first exhausting, and then heating for some hours in an open flask on the water-bath.

A determination of the amount of thiocarbimide product in one of these preparations was made, by boiling a fraction of the solution with alcoholic silver nitrate, filtering off the resultant precipitate, digesting it with strong ammonia, and weighing the residual metallic sulphide; in this manner it was ascertained that only about one-fifth of the carbonyl chloride employed had undergone conversion into thiocarbimide.

*Action of Alcohol.*—To the clear solution, obtained as described above, was added a considerable excess of nearly anhydrous alcohol; the mixture at once became warm, and on evaporation of the solvents, a yellow solid was left, together with a sticky reddish oil, most of which could be got rid of by washing with ethyl acetate. When recrystallised twice from dry benzene, the solid product was obtained in pale yellow prisms moistening slightly at  $133^{\circ}$ , and melting, with effervescence, at  $141$ — $142^{\circ}$  (corr.). It was easily soluble in alcohol or acetone and moderately so in ether or hot benzene, but insoluble in light petroleum. Cold water had no action on the finely-powdered substance, but if heated with water to near the boiling point, it slowly dissolved with effervescence, due to the escape of carbon dioxide; the solution was strongly acid to litmus, gave an intense reaction for thiocyanic acid on treatment with ferric chloride, and on cooling deposited a small quantity of white prisms melting at  $180$ — $181^{\circ}$  (uncorr.), which have not yet been identified. Warm caustic alkali readily dissolved the original substance, and the solution, when mixed with a lead salt, was strongly desulphurised on heating; silver nitrate gave with the alcoholic solution a yellowish precipitate, soluble in hot ammonia with gradual formation of silver sulphide.

A complete analysis afforded the following results:

C = 31.4; H = 3.7; N = 15.0; S = 33.8 and 34.2.  
 $C_5H_6O_2N_2S_2$  requires C = 31.54; H = 3.16; N = 14.77; S = 33.71;  
 O = 16.82 per cent.

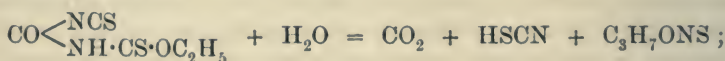
Hence, the substance is not the expected  $CO(NH \cdot CS \cdot OC_2H_5)_2$ .



which would require C=35.6; H=5.1; N=11.9; S=27.2; O=20.4 per cent. Comparing the empirical formula of the latter,  $C_7H_{12}O_3N_2S_2$ , with that found, namely,  $C_5H_6O_2N_2S_2$ , the difference is  $C_2H_6O$ ; that is, only one mol. of alcohol unites with each mol. of carbonyldithiocarbimide:



In connection with this unexpected result, it may be noted that carbonyl chloride itself does not very readily unite with more than one mol. of alcohol, but yields first ethyl chlorocarbonate,  $C_2H_5O \cdot CO \cdot Cl$ . It is probably by reason of the non-saturation of the second  $\cdot NCS$  (or  $\cdot SCN$ ) group, that the hemithiourethane is able to afford thiocyanic acid on hydrolysis:



but this explanation is only suggested provisionally, until larger quantities of material shall be forthcoming, so as to permit of the identification of the substance melting at  $180^\circ$  alluded to above.

With a view to the end mentioned, and especially in order to avoid, if possible, the tedious and rather infertile preparation of the carbonyldithiocarbimide, an attempt was made to obtain its additive compound by treating an alcoholic solution of potassium thiocyanate with carbonyl chloride. This method, however, is always an unsatisfactory one in cases where the acid chloride is readily decomposed by the alcohol (because, if the solution be used hot, the alcohol rapidly destroys the chloride, and if it be used cold, the metallic salt is only sparingly soluble, and consequently the alcohol is present in relatively very great excess); and although the constituents interacted readily with formation of potassium chloride, not a trace of the desired compound could be obtained.\* The nature of this interaction will be explained later on.

\* Crocker has recently shown (Trans., 1902, 81, 436), that from picryl chloride (which is not attacked by alcohol) and alcoholic ammonium thiocyanate, a very satisfactory yield can be obtained of an ethyl picryl picriminothiocarbonate, which appears to originate from a picrylthiocarbimide initially formed. The mechanism of this process is explained by him as follows: (1)  $PiCl + NH_4SCN = PiNCS + NH_4Cl$ . (2)  $PiNCS + PiCl = PiN:CCl \cdot SPi$ . (3)  $PiN:CCl \cdot SPi + EtOH = PiN:C(OEt) \cdot SPi$  ( $Pi = \text{picryl}$ ).

This series of changes is remarkable and interesting. For, in the first place, the present writer has repeatedly attempted to obtain picrylthiocarbimide from picryl chloride, in hydrocarbon solvents, and metallic thiocyanates, but always without success (see, for instance, Trans., 1899, 75, 390): in one experiment, the chloride, in benzene, was boiled for three days with lead thiocyanate, but no thiocarbimide product could be detected, nor did the addition of alcohol yield a trace of Crocker's compound; it is curious that the initial decomposition should occur so readily in

*Action of Aniline.*—The results which occur with bases of this class vary according to the conditions under which they are used.

In one series of experiments the aniline, diluted with benzene, was dropped slowly, and with constant stirring, into solution of carbonyl-dithiocarbimide, until the precipitation of a yellow solid just ceased; the mother-liquor was then at once poured off from the latter and set aside; in a short time further deposition of solid matter occurred, which generally contained some carbanilide; on evaporating the liquor from this to dryness, it proved to consist mainly of aniline hydrochloride. By recrystallising the yellow solid from absolute alcohol, very brilliant thin plates were obtained, having a beautiful pearly lustre; when powdered and slowly heated in a narrow tube, they softened at  $172^{\circ}$ , but quickly hardened again, and now melted, with effervescence, at  $222\text{--}223^{\circ}$  (corr.). If put into the apparatus at a few degrees above  $172^{\circ}$ , the substance ran to a clear liquid, which, almost in the act of liquefaction, resolidified, the solid melting as before at  $222\text{--}223^{\circ}$ ; this behaviour was unchanged by again recrystallising from methyl alcohol. Another portion, previously heated to the softening temperature, was recrystallised from alcohol; it now no longer softened at  $172^{\circ}$ , but melted at the higher temperature: probably these are isomeric forms of the same compound.

When dried by standing for a day or two over sulphuric acid, a partial analysis was made, the results being,  $N=15.5$ ;  $S=23.6$  per cent., or a ratio of nitrogen to sulphur of 3 to 2. It would seem, however, that the substance must, under these circumstances, retain some alcohol, for on further drying for several hours in the steam oven, the crystals lost much of their pearl-like brilliancy, and when now submitted to analysis yielded the following results, the  $N_3S_2$  ratio remaining unchanged:

Found  $C=45.3$ .  $H=3.4$ ;  $N=18.0$ ;  $S=27.3$  per cent.

$C_9H_7ON_3S_2$  requires  $C=45.51$ ;  $H=2.96$ ;  $N=17.76$ ;  $S=27.02$ ;  
 $O=6.75$  per cent.

presence of alcohol. And secondly, the combination of the thiocarbimide, as fast as it is produced, with more picryl chloride, is a very unusual kind of change: it does not occur, for instance, when benzoyl chloride or ethyl chlorocarbonate is mixed with the alcoholic solution of a thiocyanate; moreover, the writer has occasionally tried to effect the direct combination of thiocarbimides with acid chlorides, and with alkylogens—for example, phenylthiocarbimide and benzoyl chloride, with the view of obtaining the compound  $PhCO \cdot NPh \cdot CS \cdot Cl$ , or possibly  $PhN : CCl \cdot S \cdot COPh$ —but unsuccessfully.

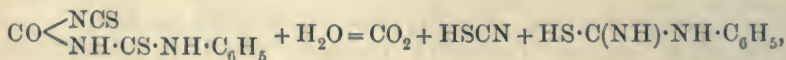
To Crocker's description it may here be added that the compound explodes when sufficiently heated; and that the contained sulphur is not withdrawn, either by ammoniacal silver nitrate, or by boiling with alkaline solution of lead. If, however, caustic alkali be added to a boiling alcoholic solution of the substance, mixed with silver nitrate and excess of ammonia, desulphurisation occurs very soon. As a rule, thiocarbonates are very easily desulphurised.



Only one mol. of aniline, therefore, unites with each mol. of carbonylthiocarbimide, when added under the conditions just described; the action in this respect being analogous to that between the thiocarbimide and alcohol (p. 87).

The dry substance becomes highly electrical on friction with a spatula; it is insoluble in light petroleum, and sparingly soluble in benzene or chloroform, but moderately easily so in hot alcohol, acetone, nitrobenzene, glacial acetic acid, or caustic potash. Its alcoholic solution yields with alcoholic silver nitrate a yellowish precipitate, scarcely soluble in ammonia, but copiously blackened on boiling with it; the potash solution, when boiled, smells distinctly of phenylthiocarbimide, and when mixed with a lead salt and warmed, is readily desulphurised.

Cold water had no action on the finely-powdered solid; the mixture was neutral to litmus, and gave not a trace of red coloration with ferric chloride. But on continued heating with water to near the boiling point, the substance gradually dissolved, with effervescence: the gas, when passed into lime-water, yielded an abundant precipitate of calcium carbonate; the lime-water smelt faintly of phenylthiocarbimide, and was somewhat desulphurised by heating with alkaline lead tartrate. The residual liquid had become strongly acid, and now gave with ferric chloride the intense, blood-red thiocyanic reaction; on cooling, it deposited a yellowish crystalline solid, easily soluble in hot, but sparingly so in cold water. The latter substance, when recrystallised a couple of times from water, using animal charcoal to decolorise it, was obtained in well-formed, pure white prisms, melting at 150—151°, having a persistent bitter taste, and giving the reactions of phenylthiourea. In the main, these phenomena are summed up by the equation:



the trace of phenylthiocarbimide being due, no doubt, to a trifling hydrolysis of the phenylthiourea. A separate experiment, in which a pure specimen of the latter was boiled with water, showed that detectable quantities of phenylthiocarbimide are thus produced.

In another series of experiments, the aniline was added rapidly, and in excess, to the solution containing the thiocarbimide (or the latter dropped into excess of aniline), whereupon a yellowish precipitate separated which was occasionally viscid, but rapidly hardened; the mixture was then set aside to concentrate at the ordinary temperature. By recrystallisation from alcohol, the solid residue was separated into (1) vitreous prisms, melting at 165—166° (corr.), with evolution of gas, and (2) needles, melting at 236°, which proved to be carbanilide. A more satisfactory method of separating these constituents is to let the mixture stand for



a while in contact with strong aqueous ammonia, and to filter off the carbanilide; on acidifying the filtrate with dilute hydrochloric acid, the other constituent separates as a flocculent precipitate, which is then to be recrystallised from alcohol. This product was insoluble in cold water, chloroform, carbon disulphide, or light petroleum; sparingly soluble in ether and benzene, moderately so in hot methyl or ethyl alcohol, and easily so in acetone, aqueous potash, or ammonia. The alcoholic solution was instantly desulphurised by ammoniacal silver nitrate; if treated with alkaline lead tartrate, a bright crimson precipitate fell, which soon darkened, even in the cold, or was blackened at once on heating, owing to the formation of lead sulphide. When boiled with water, the solid did not appear to dissolve; the mixture evolved no carbon dioxide, remained neutral to litmus, and gave no red coloration with ferric chloride. On analysis, the following results were obtained:

C=54.1; H=5.2; N=17.05; S=19.3,\* 19.4, and 19.6 per cent.  
 $C_{13}H_{11}ON_4S_2$  requires C=54.49; H=4.25; N=17.01; S=19.41;  
 O=4.84 per cent.

The formation of this compound may be represented as follows:



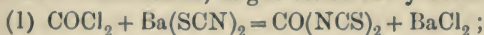
the main product being, accordingly, carbonyldiphenyldithiocarbamide; the carbanilide, which occurs in relatively small amount, sometimes in mere traces, is formed by the action of part of the aniline on the carbonyl chloride, a little of which remains dissolved in the toluene even after prolonged heating on the water-bath.

It may here be noted that phenylthiourea and carbonyl chloride, when allowed to stand together, soon interact; on heating the product with water, phenylthiocarbimide is produced, together with a pasty solid which does not appear to contain the dithiocarbamide just described. The nature of this interaction is being investigated.

It has already been mentioned that potassium thiocyanate in alcohol gave no satisfactory result when treated with carbonyl chloride. On substituting for potassium thiocyanate the much more soluble barium salt and keeping the solution cool by running water, interaction occurred at once, with precipitation of barium chloride; the filtrate had a pungent, tear-exciting odour, was copiously desulphurised by lead and silver salts, and hence, presumably, contained a thiocarbimide. This, in fact, proved to be the case, for on treating the solution with aniline, it lost the irritating smell and, on evaporation, large, well-formed crystals separated, giving the reactions of a thiourea. When recrystallised from hot alcohol, in which it is

\* This sulphur determination was made with a product melting at 160°.

moderately soluble, the substance was deposited in colourless, flattened, vitreous prisms, not much resembling those obtained from carbonyldithiocarbimide and aniline, and melting without sensible decomposition at 130—131° (corr.). In all respects, the solid answered to the description of *ab*-carboxyethylphenylthiocarbamide, m. p. 130° (Doran, Trans., 1896, 69, 326), and, on analysis, gave 12·6 of nitrogen and 14·45 of sulphur, against 12·53 and 14·31 per cent., respectively, calculated for  $C_{10}H_{12}O_2N_2S$ . The formation of this substance, under the above conditions, might conceivably occur thus:



(2)  $\text{CO(NCS)}_2 + \text{EtOH} + \text{PhNH}_2 = \text{HSCN} + \text{EtO} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ ; but this explanation does not well accord with the fact that the compound  $\text{SCN} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$  may be recrystallised from ethyl alcohol without undergoing change into carbethoxyphenylthiocarbamide; it seemed therefore more likely that the pungently smelling product was carbethoxythiocarbimide, originating through the conversion of the phosgene by the alcohol into ethyl chlorocarbonate, which, acting then on the barium thiocyanate, could afford carbethoxythiocarbimide:



Finally, the carbethoxythiocarbimide uniting with the aniline would give carbethoxyphenylthiocarbamide (ethyl phenylthioallophanate).

In order to decide experimentally between these alternative explanations, it was only necessary to cause the dissolved thiocarbimide product to interact solely with the alcohol. Because, if carbonyldithiocarbimide were present it would afford the compound  $\text{SCN} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{OEt}$ , melting at 141—142°, whilst carbethoxythiocarbimide must yield carbethoxythiourethane,  $\text{EtO} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{OEt}$ , the melting point of which lies (Doran, *loc. cit.*, 334) between 44° and 45°.

The experiment was carried out by adding a solution of carbonyl chloride to excess of barium thiocyanate dissolved in cold alcohol, whereupon barium chloride was at once precipitated; after keeping for some hours, the mixture was filtered, the pungently smelling filtrate then gently warmed and left exposed to the air in an open dish to concentrate. Presently, a yellow solid was deposited in small quantity; this was filtered off and identified as isopersulphocyanic acid. In about 10 days, the solvent had evaporated, leaving a clear, reddish-brown oil, which was dissolved in spirit and the solution then poured into water to get rid of the excess of barium thiocyanate. The resultant oil, after further washing, was dried, extracted with, and again recrystallised from, boiling light petroleum, from which, on cooling, it separated in pure white prisms melting at 43—44° and

otherwise exhibiting the properties of carbethoxythiourethane or diethyl iminothiodicarbonate.

From these results, the mechanism of the interaction is clear: the phosgene decomposes primarily with the alcohol, and the chlorocarbonate thereby formed affords with the metallic thiocyanate carbethoxythiocarbimide; this slowly combines with the alcohol, if it alone be present, or unites at once with aniline, if this be added, to produce the corresponding phenylated thiocarbimide.

Whilst the use of alcohol as solvent for the metallic thiocyanate is thus inadmissible for the synthesis of derivatives of carbonyldithiocarbimide, it may here be remarked that, so far as it has been tried, the above process answers fairly well as a method for producing the compounds of carbethoxythiocarbimide.

For reasons mentioned earlier in this paper, it is very desirable to present the metallic thiocyanate in solution to the carbonyl chloride; and as ethyl acetate was found to dissolve the potassium salt moderately freely, a small experiment was tried with these materials, but no definite compound could be obtained. The experiment was then repeated, using barium thiocyanate, dissolved in slightly warm ethyl acetate. Much heat was evolved on adding the carbonyl chloride, (8 grams  $\text{COCl}_2$ ), and barium chloride was precipitated; the filtrate was treated with aniline, concentrated, the residue washed with water to remove excess of thiocyanate, and the solid product purified by recrystallisation from alcohol. It melted at  $130\text{--}131^\circ$ , and proved to be carbethoxyphenylthiocarbamide, originating, no doubt, from the presence of much alcohol in the so-called "absolute" ethyl acetate: the mother liquor was examined, but no trace could be found of carbonyldiphenyldithiocarbamide.

*Action of p-Toluidine.*—A solution of *p*-toluidine in benzene was added to the dithiocarbimide solution until no further precipitation could be observed to occur—this required only one-third of the amount calculated from the phosgene used—the mother liquor was then treated with more toluidine, and set aside; it soon deposited a white solid, containing mere traces of sulphur: when recrystallised from a mixture of alcohol with benzene, this came down in pure white, slender, felted needles melting at  $260^\circ$ , and consisting of di-*p*-tolyl-carbamide  $\text{CO}(\text{NH}\cdot\text{C}_7\text{H}_7)_2$ :

Found  $\text{N} = 11.7$ ;  $\text{C}_{15}\text{H}_{16}\cdot\text{ON}_2$  requires  $\text{N} = 11.69$  per cent.

The precipitate first obtained was somewhat pasty, but quickly hardened; when recrystallised from a mixture of benzene with absolute alcohol, it was deposited in faintly yellow leaflets, having a brilliant pearly lustre, and closely resembling the phenyl homologue in appearance. When heated in a narrow tube, it softened a little



at about  $182^{\circ}$ , hardening again, and melting, with effervescence, at  $237^{\circ}$  (corr.); if put into the apparatus at  $190^{\circ}$ , it ran to a liquid which resolidified instantly, the solid melting sharply at  $237^{\circ}$ . On analysis :

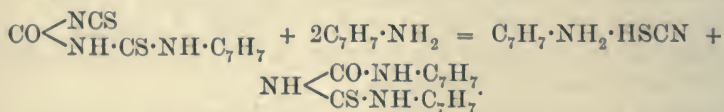
Found, N = 16.9 ; S = 25.4.

$C_{10}H_9ON_3S_2$  requires N = 16.77 ; S = 25.52 per cent.

Hence the interaction is similar to that in which aniline is used under like conditions, the product being a molecular compound of the base and dithiocarbimide,



In relation to solvents and to desulphurising agents, its behaviour generally resembles that of the phenyl homologue ; moreover, it is unaffected by cold water, but decomposed by boiling with it, yielding carbon dioxide and thiocyanic acid. A quantity, dissolved in methyl alcohol, was boiled with excess of *p*-toluidine, in order to learn whether it would yield the di-substitution derivative,  $CO(NH \cdot CS \cdot NH \cdot C_7H_7)_2$  ; it decomposed, however, yielding *p*-toluidine thiocyanate, and a substance crystallising from alcohol in white, felted needles, melting at  $192-193^{\circ}$  (corr.), and containing only 10.9 per cent. of sulphur—carbonylditolyldithiocarbamide would require 17.9 per cent. The amount was too small to permit of further examination, but the substance was probably di-*p*-tolylthiobiuret (S = 10.7 per cent.), resulting thus :

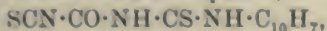


*Action of o-Toluidine.*—The dithiocarbimide used in this preparation was obtained from carbonyl chloride (in toluene) and dry barium thiocyanate ; these substances interact spontaneously with evolution of heat, but the yield of thiocarbimide is very poor, much collateral decomposition occurring, with production of carbonyl sulphide. Excess of toluidine was employed, and eventually a solid separated, melting at  $171-172^{\circ}$  (corr.), and exhibiting properties in all respects similar to those of carbonyldiphenyldithiocarbamide,  $CO(NH \cdot CS \cdot NH \cdot C_7H_7)_2$ . On analysis :

S found = 17.7.  $C_{17}H_{15}ON_4S_2$  requires S = 17.89 per cent.

*Action of  $\alpha$ -Naphthylamine.*—A granular solid fell on the addition of excess of  $\alpha$ -naphthylamine ; this was filtered off without delay, and, as it proved to be almost insoluble in water, alcohol, acetone, benzene, &c., it was repeatedly boiled up, first with alcohol, and then with a

mixture of alcohol with benzene, after which treatment a yellowish, mobile powder was left, melting, with slight evolution of gas, at  $181-182^{\circ}$  (corr.); the brownish liquid quickly resolidified (it did not, however, become perfectly dry), and now melted at  $222^{\circ}$  (corr.). From this behaviour, notwithstanding that excess of base had been used, it appeared probable that a molecular compound,



was in hand; the result of analysis showed this to be the case:

Found, N = 14.7; S = 22.55.

$\text{C}_{13}\text{H}_9\text{ON}_3\text{S}_2$  requires N = 14.65; S = 22.32 per cent.

When boiled with water alone, the substance is hydrolysed with some difficulty, the mixture becoming faintly acid, and giving with ferric chloride only a moderate red coloration. But if heated with caustic potash, free from carbonate, it is quickly hydrolysed; the solution, when treated with excess of hydrochloric acid, effervesces, owing to the escape of carbon dioxide; at the same time, it becomes turbid from separation of naphthylthiourea, and the filtrate gives an intense reaction for thiocyanic acid. Ammonia acts similarly, but in presence of dilute sulphuric acid, practically no hydrolysis occurs. From the readiness with which alkali brings about the decompositions just mentioned, it follows, of course, that the substance is easily desulphurised by alkaline lead and silver salts.

*Action of Benzylaniline.*—In order to learn whether a secondary base would unite with the dithiocarbimide, an experiment was carried out, using excess of benzylaniline dissolved in benzene. On mixing the constituents, heat was evolved, but no precipitate separated; the mixture, when concentrated by slow evaporation, formed a mass of crystals entangling a sticky oil which consisted mainly of benzylaniline. After removing the latter by washing with benzene and alcohol, the residue was twice recrystallised from boiling alcohol, in which it is moderately soluble, and was thus obtained in long, vitreous prisms having a faint yellow tinge, and melting at  $179-180^{\circ}$  (corr.) with effervescence.

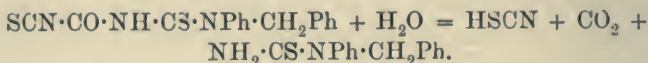
Contrary to expectation, for the dithiocarbimide had lain for nearly 24 hours in contact with excess of base, the product turned out to be the molecular additive compound  $\text{SCN} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{N}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ :

Found, S = 19.7; N = 12.9.

$\text{C}_{16}\text{H}_{13}\text{ON}_3\text{S}_2$  requires S = 19.59; N = 12.87 per cent.

When boiled with ammoniacal silver nitrate for a short time, the alcoholic solution remains perfectly clear; the solid is gradually attacked by heating with alkaline lead tartrate and black clots appear containing lead sulphide. The substance is insoluble in, and un-

affected by standing with, cold water; when boiled with it, the crystals slowly decompose, evolving carbon dioxide and changing to a translucent, half-melted, yellow solid, which now floats on the water. The latter gives with ferric chloride an intense thiocyanic reaction; the former, when recrystallised from very weak spirit, is deposited in brilliant, white needles melting sharply at  $136-137^{\circ}$ . These needles in alcoholic solution give an immediate black precipitate with ammoniacal silver nitrate and are soon desulphurised by boiling with alkaline solution of lead; they consist of  $\alpha\alpha$ -phenylbenzylthiourea (Trans., 1895, 67, 571), the formation of which, together with that of the accompanying products, may be represented thus:



The above hydrolysis is more quickly brought about by heating the parent substance with dilute potash to the temperature at which the mixture suddenly becomes finely turbid; this turbidity is due to the separation of  $\alpha$ -phenylbenzylthiourea, which is practically insoluble in water or caustic alkali. Its composition was checked by a sulphur determination:

Found, S = 13.3.  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$  requires S = 13.23 per cent.

#### *Attempt to Isolate Carbonyldithiocarbimide.*

One hundred and eight c.c. of the toluene solution, corresponding to about 20 grams of carbonyl chloride, were heated for fifteen hours with double the calculated quantity of sodium thiocyanate, finely sifted, and carefully dried. The dissolved product was separated as completely as possible from the solid residue, which, in order to avoid extreme dilution, was only given a single light washing with dry benzene. After exhausting for an hour in the cold, to get rid of some of the unchanged carbonyl chloride, the solution was distilled from a water-bath at  $90^{\circ}$ , under reduced pressure, using a Young's rod-and-disc still-head. All the solvent came over between  $35$  and  $40^{\circ}$ , at a pressure changing slowly from 40 to 33 mm., the end of the distillation being sharply marked: a turbid liquid residue, very trifling in amount, was then transferred to a small distilling flask, and the internal pressure reduced to 23 mm. On heating the flask to the temperature of boiling water, no liquid distilled over, but the contents frothed and became darker, and more solid matter appeared to separate; the process was therefore interrupted, and the liquid freed from an accompanying brownish solid by filtration through dry paper. The filtrate was a dark reddish oil, having a very pungent, tear-exciting odour,



closely resembling that of acetylthiocarbimide: it amounted to something less than three grams, and soon became turbid on keeping—a property common to almost all thiocarbimides of the acidic class.

When warmed with alkaline lead salts, or when mixed, in the cold, with ammoniacal silver nitrate, it was very copiously desulphurised; its solution in weak spirit gave with ferric chloride a strong thiocyanic reaction. The oil combined rapidly with alcohol, yielding a rather sticky crystalline solid, and united almost explosively with aniline, even when both constituents were diluted with fully an equal volume of benzene, forming a pasty solid, exhibiting the properties of a thiocarbimide. There could be little doubt that the material in hand was carbonyldithiocarbimide, but obviously still far from pure, for in addition to being highly coloured, it even yet retained some chlorine. A sulphur determination, in fact, showed it to contain just under 40 per cent. of the latter element, whilst pure  $\text{CO}(\text{NCS})_2$  would require  $\text{S} = 44.6$  per cent. The toluene distillate was collected in four fractions; all—even the last—fumed on exposure to moist air, and smelt of phosgene; and every one contained much thiocarbimidic product, giving a thick black precipitate on the addition of ammonia to the mixture of a portion with excess of silver nitrate.

The results set forth in the preceding pages are obviously very incomplete, and notably so as regards the failure of all attempts to obtain a pure specimen of carbonyldithiocarbimide itself; the difficulty in this case depends largely on the fact that, hitherto, it has not been found practicable to produce more than some four or five grams of it at a time, this small quantity becoming ultimately so diluted with various solvents, that the total bulk cannot well be kept under 150 or 160 c.c. Moreover, the solutions being contaminated, as already mentioned, with both thiocyanic acid and phosgene, the purification of the compounds obtained from them could only, as a rule, be accomplished with great loss; so that, whilst the preparations are tedious, the yield of pure material eventually obtained is anything but satisfactory.

It was originally proposed to continue these experiments, in the hope of definitely isolating this interesting "mustard-oil"; but in view of the fact that several investigators are now occupied in studying the chemistry of acidic thiocarbimide derivatives, and as some little time may elapse before the writer is free to pursue the subject mentioned, it seemed desirable to offer to the Society, without further delay, some account, even though incomplete, of such results as have been secured.

In conclusion, the author desires to express his indebtedness to

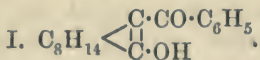
Mr. R. E. Doran for considerable assistance, especially with respect to the numerous analytical determinations which it has proved necessary to make during the course of this investigation

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QUEEN'S COLLEGE,  
CORK.

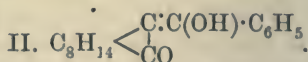
# IX.—*Studies in the Camphane Series. Part X.* *The Constitution of Enolic Benzoylcamphor.*

By MARTIN ONSLOW FORSTER.

IN recording the properties of  $\alpha$ -benzoylcamphor (Trans., 1901, 79, 987), it was pointed out that the enolic modification may have a constitution expressed by one of the formulæ



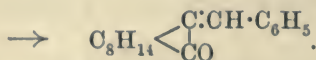
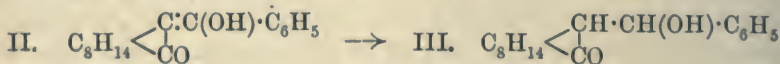
1-Hydroxy-2-benzoylcamphene.



Phenylhydroxymethylenecamphor.

The slender evidence then available appeared to favour the first of these expressions, but it was recognised that more systematic investigation was required before a definite opinion could be pronounced.

On subjecting enolic benzoylcamphor to reduction with sodium amalgam, the chief product was found to be benzylidenecamphor, which was first obtained by Haller from benzaldehyde and the sodium derivative of camphor. The result might be regarded as favourable to formula II, since benzylidenecamphor would result from the following series of changes:



Benzylidenecamphor.

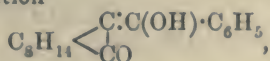
On the other hand, it can be argued that in the event of the carbonyl radicle in hydroxybenzoylcamphene becoming reduced before the ethylene linking is attacked, the product having the formula

$\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_5 \\ | \\ \text{C} \cdot \text{OH} \end{array}$  would at once assume the ketonic form indicated by formula III. The behaviour of enolic benzoylcamphor on reduction, therefore, does not reveal its constitution.

Equally indecisive is the evidence afforded by oxidation with pot-

potassium permanganate. A solution of enolic benzoylcamphor in alkali reduces that agent immediately, yielding camphoric and benzoic acids. It would be reasonable to accept this in support of formula I, were it not for the fact that benzylidenecamphor and even benzylcamphor give rise to the same products.

More definite information has been gained, however, by oxidising enolic benzoylcamphor with chromic acid. It will be recognised that camphorquinone should appear as an intermediate product from phenylhydroxymethylenecamphor, whilst 1-hydroxy-2-benzoylcamphene might be expected to pass into camphoric and benzoic acids at once. By the use of chromic acid, and also by oxidation with mercuric acetate, a very small proportion of camphorquinone has been obtained from enolic benzoylcamphor, and on the evidence of these experiments the opinion is now expressed that the last-named substance has the constitution



and must be regarded, therefore, as phenylhydroxymethylenecamphor. This view is strengthened by a comparison with hydroxymethylenecamphor,  $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C}:\text{CH}\cdot\text{OH} \\ \diagdown \text{CO} \end{array}$ , which is produced by the action of iso-

amyl formate on camphor in presence of sodium (Bishop, Claisen, and Sinclair, *Annalen*, 1894, 281, 314). Such a comparison shows that in the main these two substances resemble one another closely in properties. They behave alike towards alkylating agents, acetic anhydride, benzoyl chloride, potassium permanganate, chromic acid, and ferric chloride; moreover, whilst hydroxymethylenecamphor undergoes condensation with ammonia, yielding a substance  $\text{C}_{11}\text{H}_{17}\text{ON}$ , enolic benzoylcamphor, when heated with ammonium formate, is converted into a compound having the empirical formula  $\text{C}_{17}\text{H}_{21}\text{ON}$ . Furthermore, the trichloride of phosphorus acting on hydroxymethylenecamphor, and the pentachloride with enolic benzoylcamphor, yield substances which appear to be similarly constituted.

They differ from one another in the following respects. Hydroxymethylenecamphor dissolves in sodium carbonate, whilst phenylhydroxymethylenecamphor is soluble only in caustic alkalis. Again, hydroxylamine readily converts hydroxymethylenecamphor into an oxime, but combines with phenylhydroxymethylenecamphor very slowly, yielding a substance having the properties of an isoxazole; aniline also undergoes condensation with hydroxymethylenecamphor, but is indifferent towards benzoylcamphor.

A curious distinction, also, is presented by the compound obtained from benzoylcamphor and phosphorus pentachloride when compared with the corresponding derivative of hydroxymethylenecamphor. The

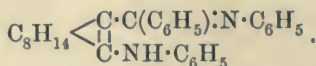


latter exchanges chlorine for other groups very readily, the former with great difficulty. Whilst alcoholic ammonia converts the latter into the compound  $C_{11}H_{17}ON$ , identical with the product from hydroxymethylenecamphor and aqueous ammonia, the substance from the phenyl derivative and alcoholic ammonia is distinct from, but isomeric with, that produced when enolic benzoylcamphor is heated with ammonium formate. It is difficult to explain the relationship between the two substances having the composition  $C_{17}H_{21}ON$ ; it seems possible, however, that their structure may be expressed by the formulæ

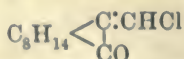


respectively.

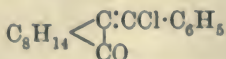
Again, whilst aniline yields with hydroxymethylenecamphor and with its chloride the anilide  $C_8H_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{NH} \cdot C_6H_5 \\ \text{CO} \end{array}$ , it has no action on phenylhydroxymethylenecamphor, and converts the chloro-derivative into a substance having the empirical formula  $C_{29}H_{30}N_2$ , and containing two aniline residues. The production of this compound is somewhat remarkable, and if taken alone would justify the formula  $C_8H_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CO} \cdot C_6H_5 \\ \text{Cl} \end{array}$  for the chloride of benzoylcamphor, because 1-chloro-2-benzoylcamphene might be expected to behave in the manner indicated, yielding a compound



It will be noted that this structure is comparable with that of phenylauramine, which is obtained also by heating a ketone with aniline hydrochloride, and therefore receives considerable support from the fact that the aniline derivative has a brilliant yellow colour and forms bright cherry-red salts; moreover, camphor itself does not undergo condensation with aniline. This behaviour towards the base is probably the strongest argument in favour of regarding the halogen atom in phenylchloromethylenecamphor as occupying a position in the camphor nucleus, but it can scarcely be said to outweigh the evidence in favour of the formula  $C_8H_{14} \begin{array}{c} \diagup \text{C} \cdot C(C_6H_5) \cdot \text{NH} \cdot C_6H_5 \\ \text{C} \cdot \text{N} \cdot C_6H_5 \end{array}$ , which follows from the probable analogy between the chlorides of hydroxymethylenecamphor and its phenyl derivative, indicated by the following formulæ:



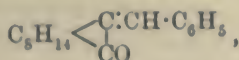
Chloromethylenecamphor.



Phenylchloromethylenecamphor.

Although the above points of resemblance are sufficiently striking, and the differences can be explained in some cases by the interchange of hydrogen and phenyl, a close consideration of the points of divergence has never precluded the possibility that they were due to the structural distinction between formulæ I and II.

A comparison of enolic benzoylcamphor with benzylidenecamphor,



throws but little light on this question. A solution of benzylidenecamphor in chloroform does not decolorise the halogen at once, but one molecular proportion of the element is absorbed in the course of several hours. Enolic benzoylcamphor decolorises bromine immediately in chloroform or acetic acid solution, yielding a mixture of the  $\alpha\alpha$ -benzoylbromocamphors (Forster and Micklethwait, *Trans.*, 1902 81, 160).

The same remark applies to their behaviour towards nitric acid, benzylidenecamphor yielding a nitrosate,  $\text{C}_{17}\text{H}_{20}\text{O}_5\text{N}_2$ , which gives Liebermann's reaction (Haller, *Compt. rend.*, 1895, 121, 35), whilst enolic benzoylcamphor is converted into  $\alpha\alpha$ -benzoylnitrocamphor (Forster and Jenkinson, *Proc.*, 1902, 252, 117). Although these distinctions in behaviour might be attributed to the difference in position of the ethylene linking in benzylidenecamphor and in hydroxybenzoylcamphene, it can be ascribed, with equal justification, to the presence of the hydroxyl group in phenylhydroxymethylenecamphor and the opportunity thus provided for elimination of hydrogen bromide.

During this investigation, attempts have been made to introduce the radicles of different acids into the camphor nucleus, but it is noteworthy that although camphor is converted into the dibenzoyl derivative with comparative readiness, it has not been possible up to the present time to convert the ketone into other acyl derivatives. In a private communication, Professor Haller has informed me that an attempt to prepare acetylcamphor has been unsuccessful, and I have failed to obtain crystalline derivatives by substituting for benzoyl chloride the chlorides of cinnamic, anisic, benzenesulphonic, phthalic, and picric acids.

## EXPERIMENTAL.

### *Oxidation of Enolic Benzoylcamphor.*

*Potassium Permanganate.*—Five grams of benzoylcamphor were dissolved in aqueous caustic potash and treated with 2 per cent. potassium permanganate solution until the red colour was permanent,

about 500 c.c. being required for the purpose. After adding a few drops of alcohol, the warmed solution was filtered, evaporated, and finally acidified with dilute sulphuric acid. The organic acids thus precipitated were dissolved in ammonia and treated with a concentrated solution of lead acetate; the camphorate and benzoate of lead were then collected and extracted with boiling water until the liquid developed only a faint coloration with sulphuretted hydrogen. All the benzoic acid was in the filtrate, whilst camphoric acid was isolated from the portion insoluble in hot water.

*Chromic Acid.*—A solution containing 10 grams of enolic benzoylcamphor in glacial acetic acid was surrounded with cold water and treated slowly with 6 grams of chromium trioxide dissolved in the minimum quantity of water. After an interval of 12 hours, the liquid was diluted, rendered alkaline with caustic soda, and extracted with ether, which formed a yellow solution; when this was evaporated and the residue distilled in a current of steam, bright yellow crystals of camphorquinone were obtained, and these, when crystallised from alcohol, melted at  $198^{\circ}$ . The amount of quinone obtained in this way weighed rather less than 1 decigram.

*Potassium Ferricyanide.*—When a solution of benzoylcamphor in caustic potash is treated with a 20 per cent. solution of potassium ferricyanide, no apparent change occurs when the first few c.c. are added; the liquid soon becomes turbid, however, and finally a colourless, flocculent precipitate is formed. The quantity of this substance varies greatly with the conditions of the experiment, which was ultimately conducted in the following manner.

Ten grams of the diketone were dissolved in excess of aqueous caustic potash and treated with 20 grams of potassium ferricyanide dissolved in 100 c.c. of water; the precipitate was filtered off as rapidly as possible with the aid of a filter pump, and washed until the filtrate gave no coloration with ferrous sulphate. When dried in air, the precipitate weighed 7.5 grams and consisted of a pale pink powder.

On treating this substance with a small quantity of cold light petroleum, the greater portion dissolved, forming a deep red solution which became filled, almost immediately, with a bulky, colourless precipitate. This product, when filtered and washed, weighed 2 grams, and after crystallisation from boiling alcohol, in which it is sparingly soluble, was obtained in small, lustrous, white needles, melting to a pink liquid at  $221^{\circ}$ :

0.1630 gave 0.4783  $\text{CO}_2$  and 0.115  $\text{H}_2\text{O}$ .  $\text{C} = 80.03$ ;  $\text{H} = 7.60$ .

$\text{C}_{17}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 79.69$ ;  $\text{H} = 7.81$  per cent.

$(\text{C}_{17}\text{H}_{19}\text{O}_2)_2$  „  $\text{C} = 80.00$ ;  $\text{H} = 7.45$  „



Determinations of the molecular weight in benzene solution gave the values 445 and 455 instead of 510 required by the formula  $C_{31}H_{50}O_4$ . Probably 2 mols. of enolic benzoylcamphor have become united by the removal of hydrogen from their hydroxyl groups, and this view is supported by the indifference of the substance towards ferric chloride and its insolubility in alkalis; it does not decolorise bromine dissolved in chloroform.

A solution containing 0.5015 gram in 25 c.c. of chloroform at  $21^{\circ}$  gave  $\alpha_D 10^{\circ}51'$  in a 2-dm. tube, whence  $[\alpha]_D +270.4^{\circ}$ .

The substance dissolves readily in chloroform or benzene, being moderately soluble in boiling alcohol or ethyl acetate; it is insoluble in light petroleum.

*Mercuric Acetate.*—Five grams of enolic benzoylcamphor were dissolved in 100 c.c. of glacial acetic acid containing 10 grams of mercuric acetate, and allowed to remain during 10 days at the ordinary temperature. The colour of the liquid, which was initially violet, gradually became brown and finally bright yellow, while mercurous acetate was precipitated in lustrous laminæ. The acid was filtered, neutralised with sodium carbonate, and distilled with steam; the pale yellow distillate was extracted with ether, and the latter, on evaporation, deposited 0.5 gram of camphorquinone.

If the solution of benzoylcamphor in acetic acid is heated with mercuric acetate on the water-bath, no camphorquinone is obtainable from the steam distillate.

### *Reduction of Enolic Benzoylcamphor.*

Several attempts have been made to convert benzoylcamphor into a reduction product which might decide the question of its constitution. Zinc dust in acetic acid has been tried without success, and sodium in boiling alcohol gives rise to a viscous oil which is slowly volatile in steam, but does not crystallise. After some preliminary experiments, the compound was reduced under the following conditions.

Fifty grams of enolic benzoylcamphor were finely powdered and dissolved in 600 c.c. of water containing 40 grams of caustic potash. The liquid was pale pink, the colour being due to a small quantity of a pink, flocculent precipitate. It is probably to this impurity that enolic benzoylcamphor owes the colour which it so frequently displays, for the alkaline liquid, after filtration through asbestos, is very pale yellow.

The clear solution was then agitated vigorously with 800 grams of 2 per cent. sodium amalgam, added in quantities of about 100 grams at a time. The oil which separated after each treatment with the amalgam rapidly became semi-solid, and was allowed to accumulate

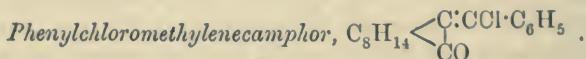
until the sodium was completely dissolved; it was then removed from the alkaline liquid, washed several times with water, and finally treated with a small quantity of cold methyl alcohol. After several days, a considerable crop of colourless crystals had separated, and these, when filtered, washed with a small quantity of cold methyl alcohol, and drained, weighed 17 grams; the substance was recrystallised first from hot alcohol and then from petroleum, which deposited colourless, transparent rhombohedra melting at  $98^{\circ}$ , and giving  $[\alpha]_D + 451^{\circ}$  in a 2 per cent. chloroform solution:

0.1771 gave 0.5477  $\text{CO}_2$  and 0.1312  $\text{H}_2\text{O}$ .  $\text{C} = 84.34$ ;  $\text{H} = 8.23$ .

$\text{C}_{17}\text{H}_{20}\text{O}$  requires  $\text{C} = 85.00$ ;  $\text{H} = 8.33$  per cent.

The empirical formula being that of benzylidenecamphor, a direct comparison was made with a specimen of that substance prepared from sodium camphor and benzaldehyde. Haller, who first obtained benzylidenecamphor by this method, gives the specific rotatory power  $[\alpha]_D + 421^{\circ}$  in toluene (*Compt. rend.*, 1899, 128, 1370), and the specimen obtained from benzoylcamphor gives  $[\alpha]_D + 420^{\circ}$  in a 2 per cent. solution in the hydrocarbon; it was further identified by conversion into the nitrosate,  $\text{C}_{17}\text{H}_{20}\text{O}_5\text{N}_2$ , which melts at  $188^{\circ}$  (Haller, *Compt. rend.*, 1895, 121, 35).

The viscous oil from which the benzylidenecamphor had been filtered remained liquid during several months, when it solidified suddenly; after being crystallised twice from light petroleum, the substance was obtained in large, transparent octahedra melting at  $50^{\circ}$ . This product was identified as  $\alpha$ -benzylcamphor, which is formed on reducing benzylidenecamphor with sodium amalgam.



Ten grams of enolic benzoylcamphor were mixed with 16 grams of phosphorus pentachloride, which acts slowly on the substance, yielding a pale yellow liquid solidifying after an interval of about one hour. At this stage it was treated several times with water, experience having shown that the yield is diminished if the treatment with water is postponed. The colourless, granular product was collected, digested with a small quantity of cold alcohol, filtered from the soluble oily bye products, and crystallised twice from boiling alcohol, in which it is readily soluble:

0.2081 gave 0.1080  $\text{AgCl}$ .  $\text{Cl} = 12.83$ .

$\text{C}_{17}\text{H}_{19}\text{OCl}$  requires  $\text{Cl} = 12.93$  per cent.

The substance is readily soluble in organic media, and separates from alcohol in long, flat, transparent prisms melting at  $100^{\circ}$ . A

solution containing 0.2505 gram in 25 c.c. of benzene at 20° gave  $n_D^{20} = 1.421$  in a 2-dm. tube, whence  $[\alpha]_D^{20} = -217^\circ$ .

The alcoholic solution gives no coloration with ferric chloride, and may be boiled with aqueous caustic soda without losing chlorine. The compound is converted into a crystalline nitro-derivative when dissolved in fuming nitric acid, but resists the action of fuming hydrobromic and concentrated sulphuric acids, and when dissolved in chloroform does not destroy the colour of bromine. If, however, the chloroform solution is allowed to remain with 1 molecular proportion of bromine in a stoppered bottle during 48 hours, the colour of the halogen is destroyed and hydrogen bromide is evolved; a portion only undergoes bromination, yielding an oil, whilst the remainder can be recovered unchanged from the residue deposited on evaporating the chloroform.

Attempts to reduce the substance were unsuccessful. Aluminium and sodium amalgams leave an alcoholic solution unchanged, whilst zinc in acetic acid and in alcoholic hydrochloric acid gives rise to oily products.

Ethyl benzoate was the only recognisable product of the action of boiling alcoholic hydroxylamine hydrochloride on phenylchloromethylenecamphor in the presence of anhydrous zinc chloride, and even this substance was not obtained in the absence of the condensing agent.

#### *Action of Aniline on Phenylchloromethylenecamphor.*

Ten grams of phenylchloromethylenecamphor were heated with 10 grams of aniline in a reflux apparatus, and when the liquid boiled, subsequent heating was limited to 4 minutes, during which period the contents of the flask assumed the colour of bromine. The product, when cold, consisted of aniline hydrochloride suspended in a brown resin, and on extracting the latter with hot petroleum, 4.5 grams of the salt were obtained, the calculated amount, supposing all the chlorine to have been removed, being 4.7 grams. The petroleum extract was treated with anhydrous calcium chloride, filtered, and evaporated, leaving a pale brown, viscous residue, which was dissolved in hot alcohol; lustrous, yellow crystals soon separated, and after an interval of one week amounted to 6.5 grams:

0.1720 gave 0.5413  $\text{CO}_2$  and 0.1187  $\text{H}_2\text{O}$ .  $\text{C} = 85.83$ ;  $\text{H} = 7.66$ .

0.2519 „ 14.7 c.c. of nitrogen at 13° and 760 mm.  $\text{N} = 6.89$ .

$\text{C}_{29}\text{H}_{30}\text{N}_2$  requires  $\text{C} = 85.71$ ;  $\text{H} = 7.39$ ;  $\text{N} = 6.89$  per cent.

The substance is insoluble in water and not very readily soluble in cold alcohol, crystallising in thin, lustrous, hexagonal plates, which are sulphur-yellow, and quite transparent; it melts at 117–118°.



Chloroform dissolves it very readily, forming a pale yellow solution, and it is also easily soluble in glacial acetic acid, which yields a bright red liquid. The alcoholic solution develops no coloration with ferric chloride, and the substance may be recovered quite unchanged after being heated with alcoholic potash during 4 hours. The derivative dissolves in hydrochloric and sulphuric acids to a deep red solution; when treated with boiling alcoholic hydrochloric acid, it yields aniline, but no definite product in addition to that base could be obtained.

Although boiling formic acid has no action on the substance, and an attempt to prepare a benzoyl derivative by the Schotten-Baumann method was equally unsuccessful, its character as a secondary base was established by the formation of a nitroso-derivative and an acetyl compound.

The *nitroso*-derivative is very readily soluble in alcohol, from which it crystallises in dark brown nodules, giving Liebermann's reaction and melting at  $118^{\circ}$  with an evolution of gas.

The *acetyl* derivative was obtained by heating the substance with acetic anhydride during 2 hours. After decomposing the anhydride with water, the product was very viscous, but became crystalline on treatment with a small quantity of warm alcohol :

0.3129 gave 18.2 c.c. of N at  $17.5^{\circ}$  and 755 mm.  $N = 6.69$ .

$C_{31}H_{32}ON_2$  requires  $N = 6.25$  per cent.

The compound dissolves very readily in boiling alcohol, from which it crystallises in transparent, canary-yellow prisms melting at  $166^{\circ}$ .

Although phenylchloromethylenecamphor readily interacts with aniline, it does not exchange chlorine for the piperidyl radicle; when heated with piperidine at  $140^{\circ}$  for 8 hours, some reaction occurs, however, for hydrogen chloride is eliminated, and the oily product slowly deposits a few crystals of enolic benzoylcamphor. The benzoyl derivative is also the sole product of the action of potassium cyanide and phenylchloromethylenecamphor in alcoholic solution at  $200^{\circ}$ ; there is no interaction at  $80^{\circ}$ .

#### *Action of Alcoholic Ammonia on Phenylchloromethylenecamphor.*

When chloromethylenecamphor is agitated with concentrated ammonia, the halogen is replaced by the amino-group, but this treatment leaves the corresponding phenyl derivative unaffected. Hot alcoholic ammonia, however, converts it into a basic substance having the empirical formula  $C_{17}H_{21}ON$ .

Five grams of phenylchloromethylenecamphor were heated with 15 c.c. of absolute alcohol saturated with dry ammonia, during 8 hours at  $150-170^{\circ}$  in a sealed tube; crystals of ammonium chloride were

produced, and from these the yellow liquid was filtered. On evaporating the alcohol, a viscous residue was obtained, which, when treated with water, soon became crystalline. A few c.c. of concentrated hydrochloric acid having been added, the liquid was filtered from unaltered phenylchloromethylenecamphor and treated with caustic potash, which gave rise to a colourless precipitate; the latter was filtered, washed, and crystallised twice from a small quantity of hot alcohol:

0.1276 gave 0.3737  $\text{CO}_2$  and 0.0950  $\text{H}_2\text{O}$ .  $\text{C} = 79.87$ ;  $\text{H} = 8.27$ .

0.3903 „ 20.7 c.c. of nitrogen at  $19^\circ$  and 755 mm.  $\text{N} = 6.05$ .

$\text{C}_{17}\text{H}_{21}\text{ON}$  requires  $\text{C} = 80.00$ ;  $\text{H} = 8.23$ ;  $\text{N} = 5.49$  per cent.

A solution containing 1.0067 grams in 25 c.c. of chloroform at  $21^\circ$  gave  $\alpha_D + 14^\circ 30'$  in a 2-dm. tube, whence  $[\alpha]_D + 180.2^\circ$ .

The base is sparingly soluble in cold alcohol, but dissolves readily in the hot liquid, and separates in hard, well-formed, transparent, highly refractive prisms; it melts at  $170^\circ$ .

Its secondary character is established by the formation of a nitroso-derivative and by the indifference of benzaldehyde, which does not undergo condensation. The base may be dissolved in hot concentrated sulphuric acid without decomposition, and also remains unchanged when boiled during 2 hours with either alcoholic hydrochloric acid or anhydrous formic acid; if, however, the action of the last-named substance is continued during 8 hours, enolic benzoylcamphor is regenerated.

An alcoholic solution does not reduce ammoniacal silver nitrate, even on boiling, but it develops an intense, blue coloration with ethereal ferric chloride.

The *picrate* crystallises from alcohol in spherical aggregates of minute, canary-yellow needles, and melts at  $157^\circ$ :

0.2250 gave 22.8 c.c. of nitrogen at  $20^\circ$  and 766 mm.  $\text{N} = 11.68$ .

$\text{C}_{23}\text{H}_{25}\text{O}_8\text{N}_4$  requires  $\text{N} = 11.54$  per cent.

The *platinichloride* is an oil. The *benzoyl* derivative crystallises from hot dilute alcohol in aggregates of silky needles melting at  $99-100^\circ$ :

0.2709 gave 10.4 c.c. of nitrogen at  $19^\circ$  and 758 mm.  $\text{N} = 4.40$ .

$\text{C}_{24}\text{H}_{25}\text{O}_2\text{N}$  requires  $\text{N} = 3.90$  per cent.

It is sparingly soluble in boiling petroleum, but dissolves readily in hot alcohol or chloroform.

*Action of Ammonium Formate on Benzoylcamphor.*

Ten grams of enolic benzoylcamphor were heated in a sealed tube with 15 grams of ammonium formate at 200—220° during 4 hours. The contents of the cold tube were under very considerable pressure, and consisted of a hard, opaque, crystalline mass and a clear, colourless liquid. If the temperature indicated is not maintained during the experiment, the tubes are found to contain unaltered benzoylcamphor. There is no appreciable formation of ammonium carbonate.

In successful experiments, the solid substance was washed with water, treated with a small quantity of cold alcohol, and filtered. After two crystallisations from a small quantity of hot alcohol, in which it is readily soluble, long, striated, hexagonal prisms were obtained melting at 118—119°. Analysis shows that the substance is isomeric with that obtained from phenylchloromethylenecamphor and alcoholic ammonia:

0.1248 gave 0.3647 CO<sub>2</sub> and 0.0923 H<sub>2</sub>O. C = 79.69; H = 8.21.

0.1790 „ 8.9 c.c. of nitrogen at 23° and 767 mm. N = 5.65.

C<sub>17</sub>H<sub>21</sub>ON requires C = 80.00; H = 8.23; N = 5.49 per cent.

A solution containing 0.5004 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D + 9^\circ 25'$  in a 2-dcm. tube, whence  $[\alpha]_D + 235.2^\circ$ .

The substance is readily soluble in concentrated hydrochloric and sulphuric acids, being precipitated from such solutions by water; it is only very slightly soluble in boiling water. An alcoholic solution has been boiled with caustic potash during two hours without undergoing change, and the compound is also indifferent towards benzaldehyde, benzoyl chloride, and nitrous acid. A solution in dilute sulphuric acid decolorises potassium permanganate immediately, producing a yellow, insoluble substance. Ferric chloride has no action on an alcoholic solution of the base.

The *picrate* crystallises slowly from mixed solutions of the base and picric acid in alcohol, forming bright yellow, transparent, hexagonal prisms remaining solid at 250°.

*Hydrolysis of the Base.*—Three grams were dissolved in 30 c.c. of absolute alcohol and heated with 10 c.c. of concentrated hydrochloric acid during four hours. Evaporation left a colourless residue which was extracted with water and filtered, the liquid depositing ammonium chloride on evaporation; the portion insoluble in water was recrystallised from a small quantity of alcohol, which deposited enolic benzoylcamphor mixed with a small quantity of the isomeride.

*Action of Bromine on the Base.*—The behaviour of the base towards bromine is remarkable, the substance which is formed appearing to have the composition C<sub>17</sub>H<sub>20</sub>ONBr<sub>5</sub>.



Two grams of the base were dissolved in 10 c.c. of chloroform and treated with a solution of bromine in the same solvent so long as the colour of the halogen was destroyed; the amount of bromine thus added corresponds to six atomic proportions. The disappearance of colour was instantaneous, and was followed almost immediately by the separation of a yellow precipitate; this, when washed with cold chloroform, in which it is insoluble, weighed 5 grams. The substance was recrystallised from boiling chloroform, separating in lustrous, orange-red plates, which melt at  $173^{\circ}$  to a deep red liquid:

0.2019 gave 0.2874 AgBr. Br = 60.59.

0.1416 „ 0.2015 AgBr. Br = 60.55.

$C_{17}H_{20}ONBr_5$  requires Br = 61.16 per cent.

The bromo-derivative is unexpectedly stable, undergoing no change in the desiccator, and crystallising from various solvents without loss of bromine. It is readily soluble in alcohol, ethyl acetate, and hot glacial acetic acid, but only sparingly so in benzene and not in petroleum; 1 gram dissolves in 50 c.c. of boiling chloroform.

When suspended in water and treated with potassium iodide, it slowly liberates iodine.

#### *Ethers of Enolic Benzoylcamphor.*

When the enolic modification of benzoylcamphor is dissolved in two parts of methyl iodide and treated with dried silver oxide, action takes place spontaneously; when this is complete and the usual process for isolating the product is carried out, a viscous, yellow oil is obtained. This substance, which has not been obtained in crystals, is indifferent towards ethereal ferric chloride.

By the action of benzyl chloride, however, a definite ether has been prepared. Fifteen grams of enolic benzoylcamphor were heated on the water-bath with 15 grams of benzyl chloride and 7 grams of dry, powdered, caustic potash during three days, at the end of which period the coloration developed by ferric chloride was very faint. A current of steam was then passed through the liquid until the odour of benzyl chloride was no longer perceptible. The colourless, viscous oil was mixed with a small quantity of cold alcohol, which precipitated the benzyl ether in minute crystals; these were drained and crystallised twice from alcohol:

0.1811 gave 0.5503 gram  $CO_2$  and 0.1225  $H_2O$ . C = 82.85; H = 7.51.

$C_{24}H_{26}O_2$  requires C = 83.23; H = 7.51 per cent.

The benzyl ether shows a tendency to form supersaturated solutions in alcohol, from which solvent it separates in large, colourless prisms,

melting at 94—95°. When the alcoholic solution is treated with ethereal ferric chloride, no coloration is developed at first, but gradually the yellow colour darkens, becoming green, and after an interval of 5 or 6 hours a purple colour appears.

A solution containing 0.5815 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D + 7^\circ 15'$  in a 2-dm. tube, whence  $[\alpha]_D + 155.8^\circ$ .

The benzyl ether dissolves readily in glacial acetic acid, methyl alcohol, or ethyl alcohol, and is very readily soluble in chloroform, benzene, or ethyl acetate; boiling petroleum also dissolves it freely, the cold solution depositing the substance in compact prisms. It is rapidly hydrolysed by alcoholic potash, yielding benzyl alcohol and enolic benzoylcamphor.

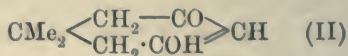
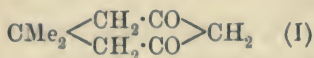
I desire to express my thanks to Miss F. M. G. Micklethwait, to whom I am indebted for the preparation of the benzoylcamphor employed in this investigation, and for a study of the benzyl ether.

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### X.—*Action of Phosphorus Haloids on Dihydroresorcins. Part I. Dimethyldihydroresorcins.*

By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR.

DIHYDRORESORCINS behave towards some reagents, notably hydroxylamine and hydrogen cyanide, as diketones (formula I), whereas towards other reagents,



they exhibit the properties of hydroxyketones (formula II), and the latter would appear to be their most usual form.

In the course of an investigation on the preparation and properties of substituted dihydrobenzenes, of which Part I has appeared (*Trans.*, 1902, 81, 821), the action of phosphorus pentachloride on substituted dihydroresorcins had to be examined, with results which seemed to render it desirable to study systematically the action of all the phosphorus haloids on these substances.

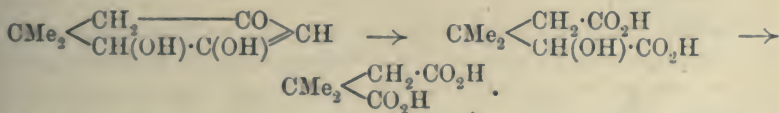
As dimethyldihydroresorcins is a well-defined crystalline compound, and is fairly readily obtained in large quantities, it was selected for the initial stages of this enquiry. It may be at once stated that it behaves as if it possessed formula II; thus, when treated with phosphorus trichloride, only the hydroxyl group is acted on, being

replaced by one chlorine atom and yielding 5-chloro-3-keto-1:1-dimethyl- $\Delta^4$ -tetrahydrobenzene,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CCl} \end{smallmatrix} \text{CH}$ . The ketonic nature of this substance is shown because it readily yields a semicarbazone; and its constitution is proved by the facts that (i) on hydrolysis with potassium hydroxide it is reconverted into dimethyldihydroresorcin; and (ii) on oxidation it gives a small quantity of *as*-dimethylsuccinic acid, but principally  $\beta\beta$ -dimethylglutaric acid and the lactone of  $\alpha$ -hydroxy- $\beta\beta$ -dimethylglutaric acid.

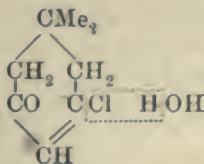
These are the same oxidation products as were obtained from 5-bromo-1:1-dimethyl- $\Delta^3$ -tetrahydrobenzene,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CH}_2 \cdot \text{CHBr} \end{smallmatrix} \text{CH}$  (Trans., 1902, 81, 824, 834), and afford additional proof of the correctness of the formula assigned to this substance. The chloroketone and the tetrahydrobenzene derivative should therefore have very similar constitutions, and the oxidation would seem to take place on the same lines. A part of the chloroketodimethyltetrahydrobenzene, for example, is oxidised, yielding  $\beta\beta$ -dimethylglutaric acid,



as the solution becomes alkaline, it is probable that the elements of hydrogen chloride are removed from a fresh portion of the chloroketone, partial oxidation taking place at the double bond so formed, giving rise to an intermediate oxidation product. From this the lactone of  $\alpha$ -hydroxy- $\beta\beta$ -dimethylglutaric acid would readily be obtained which, on further oxidation, would give *as*-dimethylsuccinic acid (*ibid.*, page 835),



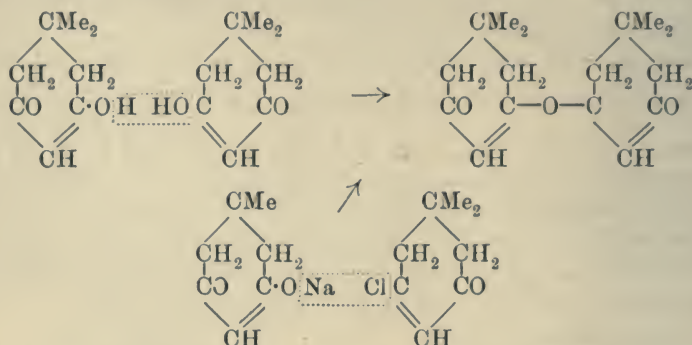
Chloroketodimethyltetrahydrobenzene appears to be very susceptible to the action of moisture, for on standing, especially if exposed to air, it slowly deposits crystals of the hydrochloride of dimethyldihydroresorcin. This is evidently a case of hydrolysis, the chloride



being decomposed under the influence of moisture into dimethyldihydroresorcin and hydrogen chloride, when these at once reunite to form the hydrochloride.



A second substance, having the formula  $C_{16}H_{22}O_3$ , is produced when phosphorus trichloride acts on dimethyldihydroresorcin, which, from its solubility in potassium hydroxide solution, and from the fact that it does not give a colour reaction with ferric chloride, would appear to be an *anhydride* of dimethyldihydroresorcin, in the formation of which the hydroxyl groups from two mols. of the dihydroresorcin have taken part.



This constitution is proved, because, on hydrolysis with alcoholic potassium hydroxide, the anhydride is quantitatively reconverted into dimethyldihydroresorcin, and also because it is formed by the action of the sodium salt of dimethyldihydroresorcin on chloroketodimethyltetrahydrobenzene. In the above instance, it is probably formed by the elimination, as hydrogen chloride, of chlorine from the chloroketone and hydrogen from the hydroxyl group of unchanged dimethyldihydroresorcin.

Dimethyldihydroresorcin yields the same chloroketodimethyltetrahydrobenzene with phosphorus oxychloride as with the trichloride, but the reaction is very much slower, for under exactly similar conditions the yield is 35 per cent. as against 66 per cent., and with the oxychloride 40 per cent. of dimethyldihydroresorcin is recovered unchanged.

In the course of this work, tribromide gives 5-bromo-3-keto-1:1-dimethyl- $\Delta^4$ -tetrahydrobenzene, a substance which closely resembles (see Crossley, 1902, 81, 821), the corresponding chloro-compound in properties. The action of phosphorus haloids on these substances has to be studied.

As dimethyldihydroresorcin is fairly readily obtained and is fairly readily obtained, the initial stages of this reaction behaves as if it possessed ferric chloride, only that presumably, the hydroxyl group in the

dihydroresorcin is replaced by one chlorine atom and the ketonic oxygen by two chlorine atoms, giving an intermediate and very unstable trichloro-derivative,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CCl}_2 \\ \text{CH}_2 - \text{CCl} \end{smallmatrix} \text{CH}$ , which readily loses hydrogen chloride, forming the above-mentioned dichlorodihydrobenzene (compare Klages and Knoevenagel, *Ber.*, 1894, 27, 3020). After many experiments, it has been found that not less than 2 mols. of the pentachloride must be used with 1 mol. of dimethyldihydroresorcin in order to obtain the pure dichlorodihydrobenzene derivative, the reason being found in the slowness of the action of phosphorus oxychloride on dimethyldihydroresorcin. If phosphorus pentachloride (1 mol.) reacts with the ketonic group first, the resulting phosphorus oxychloride would only act slowly on the hydroxyl group, whereas if the hydroxyl group is first attacked, the ketonic group remains, on which the oxychloride has no action at all; hence the need of a second mol. of phosphorus pentachloride to complete the reaction.

It was hoped that dimethyldihydroresorcin and phosphorus pentabromide would give 3:5-dibromo-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene,  $\text{CMe}_2 \begin{smallmatrix} \text{CH} : \text{CBr} \\ \text{CH}_2 \cdot \text{CBr} \end{smallmatrix} \text{CH}$ , and that possibly this substance would be more susceptible to the action of reducing agents than the corresponding dichloro-derivative, but not a trace of it has been encountered. The reaction is very complicated and has not been thoroughly worked out, although sufficient evidence has been obtained to show its general trend; it provides another example of the conversion of hydroaromatic into aromatic compounds, and when investigated may afford a ready means of obtaining substituted phenols, which are otherwise difficult of production. The detailed study of these interesting substances, however, is somewhat outside the scope of the present investigation and must be left until a future occasion.

Generally speaking, phosphorus pentabromide behaves towards dimethyldihydroresorcin as a mixture of bromine and phosphorus tribromide would do, but matters are complicated by the presence of a ketonic group, which is evidently responsible for the production, by rearrangement, of the series of bromoxylenols which have been encountered (compare Armstrong and Lowry, *Trans.* 1902, 81, 1469).

In the earliest experiments, it was found that one of the first products of the action of phosphorus pentabromide was bromodimethyldihydroresorcin (*Trans.* 1899, 75, 757), which as the reaction proceeds gradually disappears; it thus became necessary to examine the action of the phosphorus bromides on this substance, and the results obtained will be discussed first.

Phosphorus tribromide acts on bromodimethyldihydroresorcin giving rise to *mono-* and *di-bromoketodimethyltetrahydrobenzene* (see

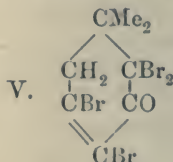
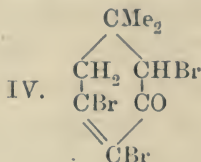
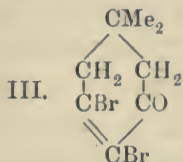
below), and also a substance which on treatment with bromine is converted into a tribromoxyleneol.

The production of bromoketodimethyltetrahydrobenzene (I) from

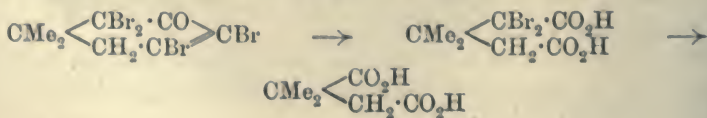


bromodimethyldihydroresorcin (II) is a reaction for which no adequate explanation is at present forthcoming. At first it was thought that there might have been some unchanged dimethyldihydroresorcin in the bromodimethyldihydroresorcin used, and the experiment was repeated with material which analysis showed to be pure, but the same result was obtained: 6 per cent. of the bromodimethyldihydroresorcin being recovered as dimethyldihydroresorcin and nearly 40 per cent. as bromoketodimethyltetrahydrobenzene.

Dibromoketodimethyltetrahydrobenzene has the constitution represented by formula III, and is the substance which it was



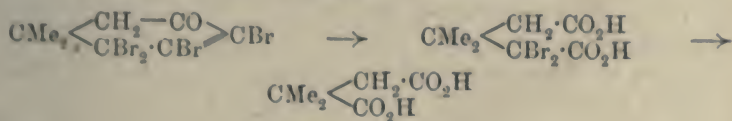
anticipated would be the sole product of the reaction. That it contains the ketonic group is shown by the fact that it readily yields a semicarbazone: but although a double linking is present bromine has no action on this portion of the molecule: it has in fact no action at all in chloroform solution in the cold, but on boiling, substitution takes place fairly readily with formation of *tribromoketodimethyltetrahydrobenzene* (formula IV), and then more slowly giving *tetrabromoketodimethyltetrahydrobenzene* (formula V). This substance seems to be the end product of the action of bromine, for on heating it with excess of bromine in chloroform solution for eight hours no further action took place. Most probably substitution takes place at the carbon atom next to the carbonyl group (compare *aa*-dibromocamphor), and although this has not been definitely proved, it has been shown that both bromine atoms are attached to the same carbon atom: for when the tetrabromo-derivative is oxidised with potassium permanganate, 69 per cent. of the calculated amount of *as*-dimethylsuccinic acid is obtained. Oxidation would naturally be expected to take place at the carbonyl group and the double linking,





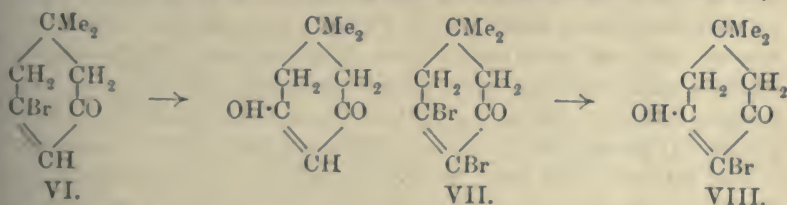
but would probably go further, converting the  $\text{CBr}_2$  group into  $\text{CO}_2\text{H}$  and thus yielding the dimethylsuccinic acid obtained.

Exactly the same result would, however, be produced by the oxidation of a substance having the alternative formula in which the bromine is associated with contiguous carbon atoms,



so that the exact constitution is not definitely proved by these experiments. Still, undoubtedly, both bromine atoms are attached to the same carbon atom, and as substitution cannot have taken place in the methyl groups, the above constitution is assigned to these derivatives as being, from experiment and from analogy, the most likely.

Monobromoketodimethyltetrahydrobenzene (formula VI below) readily absorbs bromine, but immediately gives off hydrogen bromide (suffering a transformation which has not yet been worked out), so that dibromoketodimethyltetrahydrobenzene,  $\text{CMe}_2 \begin{array}{c} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{CBr} \end{array} \text{CBr}$ , cannot be obtained by the direct action of bromine. This seems somewhat remarkable in view of the ease with which dimethyldihydroresorcin is brominated, becoming  $\text{CMe}_2 \begin{array}{c} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{C(OH)} \end{array} \text{CBr}$ , and in view of the peculiar stability of dibromoketodimethyltetrahydrobenzene. This stability is also brought out in the action of potassium hydroxide on the compound. Bromoketodimethyltetrahydrobenzene (VI) is readily acted on by hydrolytic agents with regeneration of dimethyl-



dihydroresorcin, and it was expected that dibromoketodimethyltetrahydrobenzene (VII) would behave in a similar manner, giving rise to bromodimethyldihydroresorcin (VIII), a substance which is not attacked by long boiling with alcoholic potash. Instead of this, however, the tendency seems to be to form a benzene ring by elimination of hydrogen bromide, and a liquid is obtained which gives a tribromoxenol on treatment with bromine. The formation of this tribromoxenol will be again alluded to.

The action of phosphorus pentabromide on bromodimethyldihydro-

resorcin gives rise to tribromoketodimethyltetrahydrobenzene (IV) or a mixture of this substance with the tetrabromo-derivative (V), according to the length of time that the mixture is heated. These are the sole products, no evidence being obtained of the formation of a liquid which, on treatment with bromine, gives a tribromoxylanol. This result is of importance, for, firstly, it shows that phosphorus pentabromide behaves as a mixture of bromine and phosphorus tribromide, the latter attacking the hydroxyl group, and the bromine producing substitution; and secondly, that the xylanol obtained in the action of phosphorus tribromide on bromodimethyldihydroresorcin, must be produced by rearrangement of either mono- or di-bromoketodimethyltetrahydrobenzene.

When these facts had been established, the action of phosphorus pentabromide on dimethyldihydroresorcin was resumed, and here the products vary very much according to the conditions of experiment. If the reaction proceeds for a short time only, there are formed tribromoketodimethyltetrahydrobenzene and bromodimethyldihydroresorcin, that is, compounds which would result from the action of a mixture of bromine and phosphorus tribromide. If, however, the action be continued for a longer period, a liquid, insoluble in potassium hydroxide, is obtained which, on distillation, gives a *monobromoxylanol*, a *dibromoxylanol*, and a liquid convertible into a *tribromoxylanol* (m. p. 176—177·5°) on treatment with bromine. The question of the constitution of these xylanols has not been attacked, but it seems probable that the mono- and dibromo-compounds are derivatives of

3-*o*-xylanol,  $\text{CMe} \begin{array}{c} \text{CMe} \cdot \text{C}(\text{OH}) \\ \text{CH} \text{---} \text{CH} \end{array} \text{CH}$ , for on treatment with bromine

they are both converted into a tribromoxylanol melting at 182—183°, tribromo-3-*o*-xylanol melting at 184° (Töhl, *Ber.*, 1885, 18, 2562), and, moreover, it has been shown that dichlorodimethyldihydrobenzene, which is a derivative of dimethyldihydroresorcin, readily passes into a benzene derivative (dichloro-*o*-xylene, *Trans.*, 1902, 81, 1533), in which the methyl groups are in the ortho-position relatively to one another.

One further point may be worth alluding to, and that is a clue which has been obtained as to the method of formation of these xylanols. It must be remembered that in all experiments the crude material is thoroughly washed with potassium hydroxide solution, and thus cannot contain substances of a phenolic nature; also that no xylanols have been encountered in any experiments in which distillation has not been employed. The xylanols are therefore not the primary products of the reaction, but must have been formed by decomposition and rearrangement, a fact which naturally complicates the question of their constitution. Di- and tri-bromoketodimethyltetrahydrobenzene are insoluble in cold potassium hydroxide, and each, when heated

above its melting point, loses hydrogen bromide readily, and forms a liquid which is partially soluble in potassium hydroxide, and on treatment with bromine is completely converted into the tribromoxylenol melting at 176—177.5°. So far as can be judged from experimental results, the crude material (insoluble in potassium hydroxide) obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin, consists of a mixture of di- and tri-bromoketodimethyltetrahydrobenzene dissolved in the liquid monobromo-derivative; on distillation, the di- and tri-bromo-compounds would be decomposed and suffer partial rearrangement, which would be completed by the action of bromine, a reagent which, as is well known, possesses this peculiar faculty in a marked degree (compare *Ber.*, 1893, 23, 1951; 1894, 27, 2347, and *Annalen*, 1894, 281, 98).

It is in this direction particularly that it is intended to carry out further work.

### EXPERIMENTAL.

#### *Phosphorus Trichloride and Dimethyldihydroresorcin.*

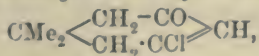
Sixty grams of dimethyldihydroresorcin (3 mols.) were suspended in 120 grams of dry chloroform and 20 grams of phosphorus trichloride (1 mol.) added; no reaction took place in the cold, and so the whole was heated on a water-bath for two and a half hours. The further method of procedure, which was adopted in all other similar cases mentioned in this paper, was as follows. After distilling off the chloroform, the residue was poured into ice-cold water and extracted with ether; the ethereal solution was thoroughly washed with caustic potash,\* carefully dried over calcium chloride, the ether evaporated, and the residue distilled in a vacuum, when all but a small residue (A) of 2.5 grams passed over constantly at 109—110° under 14 mm. pressure (amount 45 grams, yield 66 per cent.). On analysis, the following numbers were obtained:

0.1190 gave 0.2636 CO<sub>2</sub> and 0.0750 H<sub>2</sub>O. C = 60.41; H = 7.00.

0.1520 „ 0.1403 AgCl. Cl = 22.82.

C<sub>8</sub>H<sub>11</sub>OCl requires C = 60.56; H = 6.94; Cl = 22.39 per cent.

5-Chloro-3-keto-1:1-dimethyl- $\Delta^4$ -tetrahydrobenzene,



is a colourless, highly refractive, oily liquid boiling at 109—109.5°

\* The alkaline washings (16 grams) were proved to contain unaltered dimethyldihydroresorcin and some phosphorus compounds, which have not been investigated: a remark which holds good for the alkaline washings mentioned in subsequent preparations.



under 14 mm. pressure, it has a strongly marked odour of peppermint and is insoluble in water, but dissolves readily in alcohol or ether; its alcoholic solution does not give a coloration with ferric chloride. It is also insoluble in cold potassium hydroxide solution, but on boiling it slowly dissolves and is converted into dimethyldihydroresorcin.

On standing, especially if exposed to air, needle-shaped crystals separate, which, from their melting point and other properties, were proved to consist of dimethyldihydroresorcin hydrochloride (Trans., 1902, 81, 828). When the chloroketone is treated with one mol. of phosphorus pentachloride in chloroform solution, it is converted into dichlorodimethyldihydrobenzene (*ibid.*, 826), and when treated with bromine also in chloroform solution no immediate decolorisation takes place, but on standing the bromine is slowly absorbed, and on adding more bromine it is rapidly used up and torrents of hydrogen bromide are eliminated.

*Action of Halogen Acids.*—The chloroketone readily dissolves in glacial acetic acid saturated with hydrogen bromide, and on allowing the solution to stand, well-defined, rhombic plates separate, melting at 169° with decomposition and evolution of gas (dimethyldihydroresorcin hydrobromide, compare Trans., 1899, 75, 776). The crystals were readily soluble in boiling water and on cooling flat needles separated, which melted at 148° with production of a red film, and consisted therefore of dimethyldihydroresorcin.

In a similar manner, when the chloroketone is dissolved in glacial acetic acid saturated with hydrogen chloride, dimethyldihydroresorcin or its hydrochloride is obtained.

The *semicarbazone* separates almost immediately on adding semicarbazide hydrochloride (2 mols.) and the requisite amount of potassium acetate dissolved in water to an alcoholic solution of the chloroketone. It is insoluble in ether or light petroleum, but readily soluble in ethyl acetate or alcohol on boiling, and crystallises from the latter solvent in beautiful, glistening, flat needles, which melt, decompose, and give off gas at 199°:

0.1588 gave 26.6 c.c. moist nitrogen at 15° and 768 mm.  $N = 19.83$ .

$C_9H_{14}ON_3Cl$  requires  $N = 19.49$  per cent.

*Oxidation of Chloroketodimethyltetrahydrobenzene.*—Twenty grams of the chloroketone were suspended in 500 c.c. of water and a cold saturated solution of potassium permanganate was added until the colour remained permanent (75 grams  $KMnO_4$  required). The solution, which became very hot during the oxidation, was then filtered from manganese dioxide, evaporated to a small bulk, acidified, and repeatedly extracted with ether. The solid residue (20 grams), obtained by evaporating the ethereal solution, was then heated with excess of acetyl chloride

for five hours, the latter evaporated, and the whole distilled under 42 mm. pressure, when the following fractions were collected :

110—160° = few drops ; 160—200 = 5.5 grams ; residue = 9 grams.

The *fraction* 110—160° consisted of *α*-dimethylsuccinic anhydride, for, on boiling with water and saturating the solution so formed with hydrogen chloride, the corresponding acid was obtained melting at 140°.

The *fraction* 160—200° boiled for the most part between 180° and 185° and consisted of  $\beta\beta$ -dimethylglutaric anhydride melting at 123°. The acid prepared from it melted at 100° and the anilic acid at 134—135° (compare *Trans.*, 1896, 69, 1475).

The *residue* solidified completely on cooling. It was purified by repeated crystallisation from benzene, from which solvent it separated in compact masses of thick needles melting at 110.5° :

0.1846 gave 0.3568 CO<sub>2</sub> and 0.1058 H<sub>2</sub>O. C = 52.71 ; H = 6.37.

C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> requires C = 53.16 ; H = 6.33 per cent.

0.6226 required 3.85 c.c. cold *N*-sodium hydroxide. Calc., 3.94 c.c.

C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> mol. wt. calculated = 158. Found, 161.

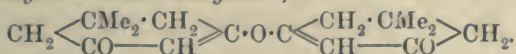
On heating the solution, a further 3.5 c.c. of *N*-sodium hydroxide were necessary for neutralisation.

This substance is evidently the lactone of  $\alpha$ -hydroxy- $\beta\beta$ -dimethylglutaric acid (compare *Trans.*, 1902, 81, 835, and Perkin and Thorpe, *Trans.*, 1899, 75, 56). When crystallised from water, it separates in masses of transparent plates which, on heating in a capillary tube, soften at about 50°, melt at 61°, and become quite clear at 82° ; they contain 1H<sub>2</sub>O, which is lost on drying in a vacuum over sulphuric acid :

1.5574 lost 0.1502 H<sub>2</sub>O. H<sub>2</sub>O = 9.64.

C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>·H<sub>2</sub>O requires H<sub>2</sub>O = 10.22 per cent.

*Dimethyldihydroresorcin Anhydride,*



—It was mentioned on page 117 that a small residue (*A*) remains on distilling chloroketodimethyltetrahydrobenzene. On standing, it solidified completely, and after purifying by crystallisation from dilute alcohol was analysed, with the following results :

0.1114 gave 0.2990 CO<sub>2</sub> and 0.0874 H<sub>2</sub>O. C = 73.21 ; H = 8.71.

C<sub>10</sub>H<sub>22</sub>O<sub>3</sub> requires C = 73.28 ; H = 8.40 per cent.

The anhydride is readily soluble in chloroform or ether in the cold, crystallises from acetone in large, hexagonal prisms and from dilute alcohol in needles melting at 99.5°. It does not impart an acid reaction to water, does not give a coloration with ferric chloride, and is insoluble in cold potassium hydroxide solution, but on heating with

alcoholic potash for 3 hours it is quantitatively converted into dimethyldihydroresorcin. Its chloroform solution does not decolorise bromine in the cold, but on warming the bromine is readily used up and hydrogen bromide is evolved.

Many attempts have been made to prepare this anhydride in larger quantity without any great success; small quantities are, however, produced by the action of phosphorus oxychloride on the potassium salt of dimethyldihydroresorcin, or by heating together the sodium salt of dimethyldihydroresorcin with chloroketodimethyltetrahydrobenzene.

*Phosphorus Oxychloride and Dimethyldihydroresorcin.*

Thirty grams of dimethyldihydroresorcin (3 mols.), 60 grams of dry chloroform, and 12 grams of phosphorus oxychloride (1 mol.) were heated for two and a half hours. The product was worked up as described on page 117, when 12 grams of a liquid boiling at  $110^{\circ}$  under 19 mm. pressure were obtained which had all the properties of chloroketodimethyltetrahydrobenzene:

0.1762 gave 0.1636 AgCl.  $\text{Cl} = 22.97$ .

$\text{C}_8\text{H}_{11}\text{OCl}$  requires  $\text{Cl} = 22.39$  per cent.

The alkaline washings yielded 12 grams of dimethyldihydroresorcin and some phosphorus compounds.

*Phosphorus Tribromide and Dimethyldihydroresorcin.*

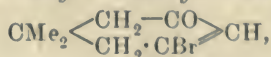
Thirty grams of dimethyldihydroresorcin (3 mols.), 60 grams of dry chloroform, and 20 grams of phosphorus tribromide were heated together for three and a half hours. On pouring into water, 0.4 gram of a solid separated, which crystallised from water or dilute sulphuric acid in fine, silken needles melting at  $296^{\circ}$ . This substance is readily soluble in the ordinary organic solvents, but the amount was too small to permit of its exact nature being determined.

The residual liquid obtained in the usual manner (p. 117) was purified by distillation in a vacuum and the bromine determined:

0.1510 gave 0.1410 AgBr.  $\text{Br} = 39.73$ .

$\text{C}_8\text{H}_{11}\text{OBr}$  requires  $\text{Br} = 39.41$  per cent.

5-Bromo-3-keto-1:1-dimethyl- $\Delta^4$ -tetrahydrobenzene,



is a heavy, colourless, refractive liquid, boiling at  $129^{\circ}$  under 25 mm. pressure and possessing a distinct odour of peppermint. It decolorises a solution of bromine in chloroform, but as in the case of the corre-



sponding chloroketone (p. 118) the initial stage of the reaction takes place slowly. On standing, it becomes slightly coloured and deposits crystals of dimethyldihydroresorcin hydrobromide melting at 168—169° with decomposition, a change which is more readily brought about by dissolving the bromoketone in glacial acetic acid saturated with hydrogen bromide.

The *semicarbazone* crystallises from alcohol in small, glistening scales melting at 190° with decomposition and evolution of gas. It is insoluble in light petroleum and only sparingly soluble in chloroform, benzene, or alcohol on boiling :

0.1662 gave 23.6 c.c. moist nitrogen at 16° and 760 mm.  $N = 16.55$ .

$C_9H_{14}ON_3Br$  requires  $N = 16.15$  per cent.

### *Phosphorus Pentachloride and Dimethyldihydroresorcin.*

The products of the action of phosphorus pentachloride (2 mols.) on dimethyldihydroresorcin (1 mol.) have already been described ; more than 80 per cent. of the calculated amount of 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., 1902, 81, 826) is obtained, and also some 3:5-dichloro-*o*-xylene (Trans., 1902, 81, 1533).

Many experiments have been made using one or one and a half mols. of phosphorus pentachloride with one mol. of dimethyldihydroresorcin, both with and without the use of chloroform as a solvent, but in no instance could the dichlorodimethyldihydrobenzene be obtained pure, as shown by numerous chlorine determinations, which invariably were from one to two per cent. low.

### *Phosphorus Tribromide and Bromodimethyldihydroresorcin.*

Bromodimethyldihydroresorcin,  $CMe_2 \begin{smallmatrix} < CH_2 - CO \\ CH_2 \cdot C(OH) \end{smallmatrix} > CBr, H_2O$ , was prepared by the method already described (Crossley, Trans., 1899, 75, 757). In this paper, it is stated that the crystalline substance melts at 173—173.5° (uncorr.), whereas, after its loss of  $1H_2O$ , it melts at 143—144°. This is an error which was unfortunately overlooked, for both the crystals containing  $1H_2O$  and the dried substances melt, decompose, and give off gas at 173—174°, and many degrees below this temperature there is a diminution in bulk (compare *Annalen*, 1902, 322, 250).

The bromodimethyldihydroresorcin used in the following experiments was carefully dried and analysed :

0.2014 gave 0.1740 AgBr.  $Br = 36.74$ .

$C_8H_{11}O_2Br$  requires  $Br = 36.53$  per cent.

Twenty-five grams of bromodimethyldihydroresorcin (3 mols.)

50 grams of dry chloroform, and 10.3 grams of phosphorus tribromide (1 mol.) were heated for six hours, during which time hydrogen bromide was slowly evolved. The alkaline washings yielded 1 gram of dimethyldihydroresorcin. The residual liquid, on standing, partially solidified, yielding 3 grams of a solid (Filtrate = A), which, after crystallisation from light petroleum, was analysed:

0.1818 gave 0.2235  $\text{CO}_2$  and 0.0584  $\text{H}_2\text{O}$ .  $\text{C} = 33.53$ ;  $\text{H} = 3.57$ .

0.1500 „ 0.1854  $\text{CO}_2$  „ 0.0464  $\text{H}_2\text{O}$ .  $\text{C} = 33.71$ ;  $\text{H} = 3.44$ .

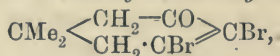
0.2238 „ 0.2996  $\text{AgBr}$ .  $\text{Br} = 56.96$ .

$\text{C}_8\text{H}_{10}\text{OBr}_2$  requires  $\text{C} = 34.04$ ;  $\text{H} = 3.54$ ;  $\text{Br} = 56.74$  per cent.

Determinations of the molecular weight by the lowering of the freezing point of a solution in benzene gave the following numbers:

Found 265 : 273. Calculated for  $\text{C}_8\text{H}_{10}\text{OBr}_2$ , mol. wt. = 282.

4 : 5-Dibromo-3-keto-1 : 1-dimethyl- $\Delta^4$ -tetrahydrobenzene,



is very soluble in the cold in ether, acetone, benzene, or chloroform, and crystallises from slightly diluted alcohol or light petroleum (b. p. 80—100°) in fern-like aggregates, or on slow crystallisation in large, octagonal pyramids melting at 95.5—96°. It is insoluble in cold potassium hydroxide, but on heating the solution becomes highly coloured and the solid gradually disappears. This alkaline liquid was extracted with ether, acidified, and again extracted; the latter ethereal solution, on evaporation, left a residue which did not solidify on standing. It was dissolved in chloroform and treated with bromine, when a solid was obtained, readily soluble in potassium hydroxide, but insoluble in sodium carbonate, and crystallising from alcohol or light petroleum in glistening needles melting at 182—183°. This substance appears to be identical with the tribromoxyleneol mentioned on page 128.

The dibromoketone is slowly attacked by cold potassium permanganate; it does not decolorise a solution of bromine in chloroform in the cold, but on heating the chloroform solution of one mol. of the substance with one mol. of bromine, hydrogen bromide is readily evolved, and after 15 minutes the whole of the bromine disappears. The solid obtained on evaporating the chloroform melted at 106° after crystallisation and was identical with the tribromoketodimethyltetrahydrobenzene described on page 124:

0.2140 gave 0.3358  $\text{AgBr}$ .  $\text{Br} = 66.77$

$\text{C}_8\text{H}_9\text{OBr}_3$  requires  $\text{Br} = 66.48$  per cent.

When very rapidly heated in a good vacuum, dibromoketodimethyl-

tetrahydrobenzene may be distilled with only slight decomposition, but on slowly heating, especially in air, it is decomposed with evolution of hydrogen bromide.

One gram of the substance was heated in a sulphuric acid bath at  $175-180^{\circ}$  until the whole of the hydrogen bromide had been evolved. The residual, slightly brown liquid (0.7 gram) did not solidify on standing, and was only to a small extent soluble in potassium hydroxide. It was dissolved in chloroform and bromine added, when the latter was rapidly used up and torrents of hydrogen bromide were eliminated. The chloroform solution left, on evaporation, 1 gram of a solid residue which crystallised from light petroleum (b. p.  $60-80^{\circ}$ ) in glistening needles melting at  $176-177.5^{\circ}$ . It was readily soluble in potassium hydroxide, but insoluble in sodium carbonate solution and consisted of the tribromoxylene described on page 128.

The *semicarbazone* separates slowly on adding the requisite quantities of semicarbazide hydrochloride and potassium acetate dissolved in water to an alcoholic solution of dibromoketodimethyltetrahydrobenzene:

0.1572 gave 16.7 c.c. moist nitrogen at  $20^{\circ}$  and 77.5 mm.  $N = 12.40$ .

$C_9H_{13}ON_3Br_2$  requires  $N = 12.39$  per cent.

It is insoluble in cold ether or light petroleum, but readily soluble in cold chloroform, and crystallises from alcohol in masses of hair-like needles melting at  $202^{\circ}$  with decomposition and evolution of gas.

The *filtrate* A (page 122) showed no sign of solidifying after long standing, and was therefore distilled in a vacuum, during which process hydrogen bromide was continuously evolved. The following fractions were collected under 28 mm. pressure:

130— $135^{\circ} = 2$  grams; 135— $145^{\circ} = 6$  grams; 145— $160^{\circ} = 2$  grams;  
160— $185^{\circ} = 6$  grams.

The accompanying sketch is of an apparatus which has been found very useful for fractional distillation in a vacuum, especially where only small quantities of liquid have to be dealt with. By means of the small stoppered funnel A, a fraction of a particular boiling point can be introduced into the distillation flask at any moment without breaking the vacuum.



The *fraction* 130— $135^{\circ}$  solidified completely on standing, forming crystals which melted at  $168-169^{\circ}$  with decomposition, and on boiling with water gave dimethyldihydroresorcin; it must therefore have consisted of the hydrobromide of this substance.

The *fraction* 135— $145^{\circ}$  consisted of an almost colourless liquid with a marked odour of peppermint. The boiling point is approximately



that of bromoketodimethyltetrahydrobenzene (page 120), and the identity of the two substances was established by preparation of the semicarbazone melting at 189—190° (found, N = 16·10, Br = 30·89; calc., N = 16·15, Br = 30·77 per cent.), and of dimethyldihydroresorcin hydrobromide, melting at 168—169° with decomposition.

The *fraction* 145—160° consisted of a mixture of the constituents of the fractions of lower and higher boiling point.

The *fraction* 160—185° was partially soluble in potassium hydroxide solution, but did not solidify on standing. It was dissolved in chloroform and treated with bromine, when a solid was obtained which was readily soluble in potassium hydroxide, but insoluble in sodium carbonate solution, and crystallised from light petroleum in glistening needles melting at 176—177·5°:

0·2060 gave 0·3254 AgBr. Br = 67·19.

$C_8H_7OBr_3$  requires Br = 66·85 per cent.

This substance is evidently identical with the tribromoxyleneol mentioned on page 128.

#### *Phosphorus Pentabromide and Bromodimethyldihydroresorcin.*

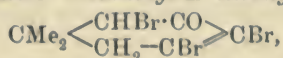
In the first experiment, 5 grams of bromodimethyldihydroresorcin, 20 grams of phosphorus pentabromide, and 50 grams of dry chloroform were used. On adding the pentabromide, bromine was set free, and the amount increased rapidly on first heating the mixture, but was gradually used up as the reaction proceeded. The mixture was heated for one hour, during which time much hydrogen bromide was evolved. After working up the product in the usual way, 3·4 grams of a thick liquid was obtained which rapidly solidified. It was purified by crystallisation from dilute alcohol and analysed:

0·1871 gave 0·1842  $CO_2$  and 0·0428  $H_2O$ . C = 26·85 : H = 2·54.

0·2116 „ 0·3310 AgBr. Br = 66·54.

$C_8H_9OBr_3$  requires C = 26·59 ; H = 2·49 ; Br = 66·48 per cent.

2 : 4 : 5-Tribromo-3-keto-1 : 1-dimethyl- $\Delta^4$ -tetrahydrobenzene,



is very readily soluble in the cold in chloroform, benzene, or acetone, and fairly readily so in alcohol or light petroleum (80—100°) on warming, and separates from the last-named solvent in fern-like aggregates, or on slow crystallisation in large, rectangular plates melting at 105·5—106°. When heated above its melting point, hydrogen bromide is evolved. Some of the substance was maintained at a temperature of 175—180°, until no more gas was eliminated, and the slightly

coloured liquid residue, which did not solidify on standing and was only partially soluble in potassium hydroxide, was dissolved in chloroform and treated with bromine, when the latter rapidly disappeared and hydrogen bromide was evolved. The solid residue left on evaporating the chloroform crystallised from light petroleum (b. p. 60—80°) in glistening needles melting at 176—177·5°, and was identical in all its properties with the tribromoxyleneol mentioned on page 128.

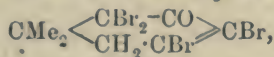
Tribromoketodimethyltetrahydrobenzene is insoluble in cold potassium hydroxide solution, is slowly attacked by potassium permanganate, and does not decolorise a solution of bromine in chloroform in the cold, although on warming the bromine gradually disappears and hydrogen bromide is evolved. The solid residue obtained by this treatment was purified by crystallisation from light petroleum (b. p. 60—80°) and analysed :

0·1510 gave 0·1224 CO<sub>2</sub> and 0·0286 H<sub>2</sub>O. C = 22·10 ; H = 2·10.

0·1302 „ 0·2238 AgBr. Br = 73·14.

C<sub>8</sub>H<sub>8</sub>OBr<sub>4</sub> requires C = 21·82 ; H = 1·82 ; Br = 72·72 per cent.

2 : 2 : 4 : 5·Tetrabromo-3-keto-1 : 1-dimethyl-Δ<sup>4</sup>-tetrahydrobenzene,



is very readily soluble in the cold in chloroform, benzene, or ether, and readily so in alcohol or light petroleum on warming, separating from the last-named solvent in stout needles or on slow crystallisation in large, four-sided prisms melting at 117·5—118°. It is insoluble in potassium hydroxide solution and is not further acted on by bromine.

*Oxidation of Tetrabromoketodimethyltetrahydrobenzene.*—Five grams of the substance were suspended in 100 c.c. of water and a saturated solution of potassium permanganate added. As the reaction took place extremely slowly in the cold, the whole was heated on a water-bath, in which case the oxidation was complete in about twelve hours, and during its earlier stages bromine was freely evolved. The solution was filtered from manganese dioxide, evaporated to a small bulk, acidified with sulphuric acid, and repeatedly extracted with ether. On evaporating the ethereal solution, a solid residue (1·1 grams ; calc., 1·6 grams) was obtained which melted at 136—137° and, after crystallisation from water saturated with hydrogen chloride, at 140°.

*α*-Dimethylsuccinic acid melts at 140—141° and the identity of the two substances was further proved by preparing the anilic acid, which crystallised from methyl alcohol in nacreous needles melting at 186° (compare Trans., 1899, 75, 861).

In a second experiment, using 25 grams of bromodimethyldihydroresorcin, 100 grams of phosphorus pentabromide and 150 grams of

dry chloroform, 20 grams of a solid were obtained, which, after repeated crystallisation, melted sharply at  $83.5-84^{\circ}$ , and gave numbers on analysis indicating that it was a mixture of tri- and tetra-bromoketodimethyltetrahydrobenzene:

Found C = 24.01 : 23.90 ; H = 2.51 : 2.30 ; Br = 70.40 : 70.54 per cent.

$C_8H_9OBr_3$  requires C = 26.59 ; H = 2.49 ; Br = 66.48 per cent.

$C_8H_8OBr_4$  „ C = 21.82 ; H = 1.82 ; Br = 72.72 „

It was therefore dissolved in chloroform and treated with bromine until absorption was complete, when the pure tetrabromoketone, melting at  $117.5-118^{\circ}$ , was obtained:

0.2060 gave 0.3530 AgBr. Br = 72.91.

$C_8H_8OBr_4$  requires Br = 72.72 per cent.

In other experiments, the crude material melted at  $110^{\circ}$  and  $101^{\circ}$ , and in both cases, on further treatment with bromine, it was completely converted into the tetrabromo-derivative melting at  $118^{\circ}$ .

### *Phosphorus Pentabromide and Dimethyldihydroresorcin.*

*Experiment I.*—Five grams of dimethyldihydroresorcin were suspended in 30 grams of dry chloroform and 31 grams of phosphorus pentabromide added. On warming on the water-bath, the dimethyldihydroresorcin quickly went into solution and hydrogen bromide and bromine were set free in large quantity; the latter was, however, rapidly used up again. After heating for ten minutes a solid was thrown out of solution, and at this point the reaction was stopped. The solid was filtered and crystallised from dilute alcohol, from which it separated in glistening scales, melting at  $173-174^{\circ}$ , and as the following bromine determination in the dried substance shows, consisted of bromodimethyldihydroresorcin:

0.2716 gave 0.2350 AgBr. Br = 36.81.

$C_8H_{11}O_2Br$  requires Br = 36.53 per cent.

The amount produced was 4.2 grams, corresponding to 2.7 grams of dimethyldihydroresorcin.

The filtrate from the solid was worked up in the usual way, when 2 grams of a substance were obtained crystallising from light petroleum in fern-like aggregates melting at  $105.5-106^{\circ}$ , and consisting of tribromoketodimethyltetrahydrobenzene (see p. 124).

0.1686 gave 0.1642  $CO_2$  and 0.0398  $H_2O$ . C = 26.56 ; H = 2.62.

0.2010 „ 0.3140 AgBr. Br = 66.46.

$C_8H_9OBr_3$  requires C = 26.59 ; H = 2.49 ; Br = 66.48 per cent.

*Experiment II.*—Twenty-five grams of dimethyldihydroresorcin



(1 mol.), 77 grams of phosphorus pentabromide (1 mol.), and 150 grams of dry chloroform were heated for three and a half hours, and then worked up in the usual manner. The residue did not solidify and was therefore distilled under 26 mm. pressure when the following fractions were obtained :

130—140° = 13 grams; 140—150° = 4 grams; 150—160° = 3·8 grams  
160—175° = 12·5<sup>g</sup> grams.

The fraction 130—140° consisted of bromoketodimethyltetrahydrobenzene (p. 120). It had about the same boiling point, the same characteristic odour of peppermint, gave a semicarbazone crystallising from alcohol in small, glistening scales melting at 190°, and was converted into dimethyldihydroresorcin hydrobromide (m. p. 168—169°) on allowing it to stand in contact with a saturated solution of hydrogen bromide in glacial acetic acid.

The fraction 160—175° solidified partially on standing. The separated solid after crystallisation from light petroleum melted at 60—72°, but the amount was too small to permit of a substance of definite melting point being separated by fractional crystallisation.

The liquid from these crystals did not solidify on standing, and on treatment with bromine was completely converted into the tribromoxylenol melting at 176—177·5° (p. 128). The fractions 140—150° and 150—160° consisted of a mixture of the constituents of the fractions of lower and higher boiling point.

*Experiment III.*—Thirty grams of dimethyldihydroresorcin (1 mol.), 185 grams of phosphorus pentabromide (2 mols.), and 150 grams of dry chloroform were heated for three-quarters of an hour and then worked up as described in experiment I (p. 126). The amount of bromodimethyldihydroresorcin obtained was 23 grams, corresponding to 15 grams of dimethyldihydroresorcin.

The residual liquid was distilled in a vacuum, when hydrogen bromide was evolved; under 23 mm. pressure, the whole passed over between 175° and 186° (19 grams), and, on standing, a solid (4 grams) separated (filtrate = A), which was crystallised from dilute alcohol and analysed :

0·1632 gave 0·2056 CO<sub>2</sub> and 0·0452 H<sub>2</sub>O. C = 34·35; H = 3·07.

0·1168 „ 0·1586 AgBr. Br = 57·77.

C<sub>8</sub>H<sub>8</sub>OBr<sub>2</sub> requires C = 34·29; H = 2·86; Br = 57·14 per cent.

This *dibromoxylenol*, C<sub>8</sub>HMe<sub>2</sub>Br<sub>2</sub>·OH, of which the constitution is at present uncertain, is insoluble in sodium carbonate solution, but readily soluble in cold potassium hydroxide, chloroform, benzene, acetone, or ether, and crystallises from slightly diluted alcohol in long, glistening needles melting at 96·5°. When treated with bromine in

chloroform solution, a tribromoxylanol melting at 182—183° is obtained (see below).

The *filtrate* A, on treatment with bromine, was completely converted into the tribromoxylanol melting at 176—177·5° (see below).

*Experiment IV.*—The same amounts of materials were employed as in Experiment III, but the heating was continued for three and a half hours. No bromodimethyldihydroresorcin was obtained, and the residual liquid gave the following fractions when distilled under 28 mm. pressure :

130—170° = 3 grams ; 170—180° = 3 grams ; 180—193° = 5 grams ;  
193—197° = 20·3 grams.

The *fraction* 193—197° solidified partially on standing. The separated solid (*filtrate* = A) was purified by fractional crystallisation from light petroleum (b. p. 40—60°) and the least soluble portion melting at 84° analysed :

0·1505 gave 0·2632 CO<sub>2</sub> and 0·0608 H<sub>2</sub>O. C = 47·69 ; H = 4·49.

0·2008 „ 0·1902 AgBr. Br = 40·30.

C<sub>8</sub>H<sub>9</sub>OBr requires C = 47·76 ; H = 4·48 ; Br = 39·80 per cent.

This *monobromoxylanol*, C<sub>8</sub>H<sub>9</sub>Me<sub>2</sub>Br·OH, is readily soluble in potassium hydroxide solution, alcohol, benzene, acetone, or chloroform, but insoluble in sodium carbonate, and crystallises from light petroleum or formic acid in radiating clusters of long, white, glistening needles melting at 83·5—84°. When treated with bromine, it is converted into a *tribromoxylanol* melting at 182—183°, which may be identical with the tribromo-derivative of 3-*o*-xylanol melting at 184°.

The solid remaining after the separation of the monobromoxylanol melted between 62° and 70° and probably consisted of a mixture of mono- and dibromo-xylanol (m. p. 84° and 96·5°), as a small quantity of the latter was separated, and on treatment with bromine the tribromo-derivative melting at 182—183° was obtained.

The *filtrate* A was treated with bromine in chloroform solution, when the bromine was rapidly absorbed and torrents of hydrogen bromide eliminated, the whole becoming semi-solid. The chloroform was evaporated, the residue spread on porous plate, purified by crystallisation from light petroleum, and analysed :

0·1630 gave 0·1616 CO<sub>2</sub> and 0·0322 H<sub>2</sub>O. C = 27·04 ; H = 2·26.

0·2302 „ 0·3628 AgBr. Br = 67·02.

C<sub>8</sub>H<sub>7</sub>OBr<sub>3</sub> requires C = 26·74 ; H = 1·95 ; Br = 66·85 per cent.

This *tribromoxylanol* is insoluble in sodium carbonate but readily soluble in cold potassium hydroxide, ether, chloroform, acetone, or benzene, and crystallises from light petroleum (60—80°) or alcohol in

long silken needles melting at  $176-177.5^{\circ}$ . The action of phosphorus pentabromide on this substance was tried in the hope of obtaining a tetrabromoxylene of known constitution, but at a temperature of  $180^{\circ}$ , the tribromoxylene is only very slightly acted on.

The *fraction*  $130-170^{\circ}$  contained bromoketodimethyltetrahydrobenzene, and the *fractions*  $170-193^{\circ}$  on treatment with bromine gave a considerable quantity of the tribromoxylene melting at  $176-177.5^{\circ}$ .

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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## XI.—*A Reaction of some Phenolic Colouring Matters.* *Part II.*

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CERTAIN phenolic dye-stuffs are known to decompose potassium acetate in the presence of alcohol with the formation of mono-substituted salts (Trans., 1899, 75, 433). The present work was undertaken with the object of determining whether all dye-stuffs of the mordant class react in this manner, and with the hope of gaining a clearer insight into the nature of this reaction. As a result, numerous typical compounds of this class have now been examined, all of which possess this property, or yield additive products with the acetate. Of the colouring matters studied, the majority have been isolated from natural sources or from such commercial preparations as were available.

### *Gallacetophenone.*

It was previously stated (*loc. cit.*) that with potassium acetate this 1:2:3-trihydroxyacetophenone gave a colourless salt, but the analysis of distinct preparations were not concordant. Analyses of products obtained in subsequent experiments gave percentages of potassium ranging from 14.79 to 13.09, numbers which are not in harmony with those required for a pure salt. It was eventually found that two distinct salts are produced together in this manner unless special precautions are taken.



*Monopotassium Gallacetophenone*.—Two grams of gallacetophenone dissolved in 20 c.c. of absolute alcohol were rapidly treated at the boiling point with 20 c.c. of a saturated solution of potassium acetate in absolute alcohol, and the fine, yellow, crystalline precipitate which formed was collected while hot, washed with absolute alcohol, and dried at 100°. The air-dried substance does not lose water of crystallisation at 100°:

0.5194, heated at 160°, lost 0.0435 H<sub>2</sub>O. H<sub>2</sub>O = 8.37.

0.5187           "           "           0.0415 H<sub>2</sub>O. H<sub>2</sub>O = 8.00.

0.4772, dried at 160°, gave 0.2012 K<sub>2</sub>SO<sub>4</sub>. K = 18.89.

0.4759           "           "           0.1979 K<sub>2</sub>SO<sub>4</sub>. K = 18.64.

C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>K, H<sub>2</sub>O requires H<sub>2</sub>O = 8.03 per cent.

C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>K           "           K = 18.92           "

It forms pale yellow, glistening needles, and is sparingly soluble in boiling alcohol, but dissolves somewhat readily in boiling water. From the aqueous solution, it crystallises out unchanged on cooling, and in this respect resembles the corresponding alizarin salt, but differs from those of morin, quercetin, &c., which are decomposed by boiling water.

Nencki and Sieber (*J. pr. Chem.*, 1881, [ii], 23, 546) obtained from gallacetophenone, by means of alcoholic potash, a salt, C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>.KHO. An examination of this compound showed it to be identical with that produced by potassium acetate:

Found, H<sub>2</sub>O = 7.97, 7.74, and in salt dried at 160°, K = 18.79, 18.74 per cent.

*Barium Salt*.—This is readily prepared by adding barium chloride to a hot aqueous solution of the potassium compound. It consists of pale yellow needles, sparingly soluble in water:

Found (salt dried at 160°), H<sub>2</sub>O = 6.58. Ba = 28.90.

C<sub>16</sub>H<sub>14</sub>O<sub>8</sub>Ba requires Ba = 29.16 per cent.

*Monosodium gallacetophenone* can be prepared in a similar way to the potassium salt by employing either (a) alcoholic sodium acetate, or (b) alcoholic soda. When dried at 160°, it loses 1 mol. of water of crystallisation:

(a) Found, H<sub>2</sub>O = 8.67, 8.53. Na, in salt dried at 160° = 12.03, 12.15.

C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>Na, H<sub>2</sub>O requires H<sub>2</sub>O = 8.65 per cent.

C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>Na           "           Na = 12.10           "

It forms a pale yellow, crystalline powder consisting of minute leaflets, and is not decomposed by boiling water. From its aqueous solution, on slow cooling, it is deposited in the form of cubes resembling the crystals of cane sugar.

*Potassium Trigallacetophenone*.—If alcoholic potassium acetate is added drop by drop to a boiling saturated solution of gallacetophenone in the same solvent, the mixture becomes semi-solid owing to the separation of colourless needles; these were collected on the pump and washed with alcohol. The air-dried product does not lose water of crystallisation at  $100^{\circ}$ :

Found, K = 7.46, 7.29, and 7.40.

$C_{24}H_{23}O_{13}K$  requires K = 7.19 per cent.

It forms a glistening mass of flat needles or leaflets which can be crystallised from water unchanged, and is not a mixture, as continued washing with alcohol does not affect its composition.

The same compound (K = 7.09 per cent.) is readily prepared by dissolving gallacetophenone in a boiling aqueous potassium acetate solution. Aqueous sodium acetate solution, however, does not react with gallacetophenone, the unaltered colouring matter being redeposited on cooling.

By adding barium chloride to a boiling aqueous solution of the compound and cooling, a barium salt separated in colourless needles which were washed with water. When air-dried, it does not lose water of crystallisation at  $100^{\circ}$ :

Found, Ba = 12.87 and 13.06.

$C_{48}H_{46}O_{24}Ba$  requires Ba = 12.02 per cent.

This is slowly decomposed at  $160^{\circ}$ , some gallacetophenone subliming.

*Methylation of Monopotassium Gallacetophenone*.—When suspended in boiling methyl alcohol, this salt was slowly attacked by methyl iodide, a clear solution usually resulting after digestion for 6 hours. The excess of iodide and alcohol was now removed, the residue extracted with ether, and the ethereal liquid evaporated. The crystalline product consisted of the required ether contaminated with colouring matter, and the latter was removed, in the form of an insoluble lead salt, by adding lead acetate to a boiling aqueous solution of the mixture. By decomposing the pale yellow precipitate with sulphuric acid, removing the lead sulphate by decantation, and extracting the clear liquid with ether, this colouring matter was recognised as gallacetophenone by means of its melting point,  $166-168^{\circ}$ , and other tests. The filtrate from the lead precipitate deposited, on cooling, long needles of the methyl ether, which, after recrystallisation from benzene, melted at  $132-133^{\circ}$ :

0.1003 gave 0.2177  $CO_2$  and 0.0475  $H_2O$ . C = 59.19; H = 5.26.

0.1008 „ 0.1313 AgI.  $CH_3$  = 8.31.

$C_9H_{10}O_4$  requires C = 59.34; H = 5.49;  $CH_3$  = 8.24 per cent.

*Gallacetophenone monomethyl ether*,  $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_3$ , is readily soluble in boiling water, and soluble in alkaline solutions with a pale yellow coloration. When crystallised from water, it is colourless, and contains 1 mol. of water of crystallisation (found  $\text{H}_2\text{O} = 8.95$ ); this is removed at  $100^\circ$ , and the substance has then a pale yellow colour.

It does not dye mordanted calico, gives no precipitate with aqueous lead acetate, and no coloration with ferric chloride; with alcoholic lead acetate, however, a gelatinous precipitate is formed which is readily soluble in water. When prepared in the above manner, the yield is exceedingly poor, and is never more than 10 per cent. of the calculated quantity.

The *acetyl* derivative,  $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_2 \cdot \text{CO} \cdot \text{CH}_3$ , prepared in the usual manner, crystallised from alcohol in colourless, prismatic needles melting at  $146-148^\circ$ :

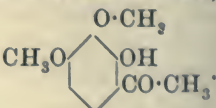
0.1125 gave 0.2415  $\text{CO}_2$  and 0.0555  $\text{H}_2\text{O}$ .  $\text{C} = 58.54$ ;  $\text{H} = 5.48$ .

$\text{C}_{13}\text{H}_{14}\text{O}_6$  requires  $\text{C} = 58.64$ ;  $\text{H} = 5.26$  per cent.

To be certain that this was the diacetyl derivative, it was decomposed with boiling sodium carbonate solution, and the product of the reaction identified as the gallacetophenone monomethyl ether. This was necessary owing to the behaviour of resacetophenone on acetylation, which forms acetoxyacetyl- $\beta$ -methylchromone in this manner, although more prolonged digestion is required (Kostanecki and Rózycki, *Ber.*, 1901, 34, 102).

By similar methods, a gallacetophenone monoethyl ether was prepared from the monopotassium salt; it crystallised in pale yellow needles melting at  $102^\circ$ .

*Gallacetophenone Dimethyl Ether*,  $\text{C}_8\text{H}_6\text{O}_2(\text{O} \cdot \text{CH}_3)_2$ .—An earlier experiment showed (*Trans.*, 1895, 67, 997) that on methylation gallacetophenone gave a dimethyl ether exclusively, and consequently contained only one hydroxyl group in the ortho-position relatively to the carbonyl group. Further investigation showed that this was the case,

and doubtless this substance has the constitution   $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3(\text{OH})(\text{CO} \cdot \text{CH}_3)$ .

It formed colourless prisms melting at  $77-78^\circ$ :

0.1026 gave 0.2292  $\text{CO}_2$  and 0.0584  $\text{H}_2\text{O}$ .  $\text{C} = 60.92$ ;  $\text{H} = 6.32$ .

0.1320 „ 0.3104  $\text{AgI}$ .  $\text{CH}_3 = 15.00$ .

$\text{C}_{10}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 61.22$ ;  $\text{H} = 6.12$ ;  $\text{CH}_3 = 15.30$  per cent.

To determine if gallacetophenone monomethyl ether gave the same dimethyl ether on further methylation, 0.8 gram, dissolved in a solution of 0.4 gram of potassium hydroxide, was heated in methyl



alcohol with excess of methyl iodide at  $100^{\circ}$  in a sealed tube for 5 hours. The main product of the reaction crystallised in colourless prisms melting at  $77-78^{\circ}$ , and was identical with gallacetophenone dimethyl ether.

It was thus evident that the methoxy-group in this monomethyl ether must exist in the meta- or para-position relatively to the carbonyl group, but, unfortunately, all attempts to solve this point have been unsuccessful at present. It seemed possible, for instance, that a monoether of pyrogallol could be converted into a gallacetophenone ether, which might be identical or otherwise with that prepared from gallacetophenone itself; and, on the other hand, could the pyrogallol ether be converted by means of phthalic anhydride into an anthragallol compound, the position of the methoxy-group would probably be ascertained by the absence of dyeing property or otherwise. Such experiments as were carried out resulted in the elimination of the methyl or ethyl group as part of the reaction and were thus abortive. It has been shown, however, that the monopotassium salts of alizarin and anthragallol on methylation give products containing the methoxy-group in the para-position relatively to one carbonyl group, and it is therefore likely that the gallacetophenone ether is similarly constituted.

During this work, some quantity of a pyrogallol monoethyl ether,  $C_6H_3(OH)_2 \cdot O \cdot C_2H_5$ , was prepared by digesting a mixture of 30 parts of pyrogallol, 15 parts of potassium hydroxide, 60 parts of ethyl iodide, and 300 parts of alcohol at the boiling point. The product soluble in alkali was distilled, the distillate dissolved in benzene, and the crystals which separated on standing purified by recrystallisation from the same solvent. This substance melted at  $102-104^{\circ}$  and is most probably identical with that described by Benedikt (*Ber.*, 1876, 9, 125), which was prepared by digesting pyrogallol with alcoholic potash and potassium ethylsulphate, and melted at  $95^{\circ}$ :

0.1286 gave 0.2924  $CO_2$  and 0.0670  $H_2O$ .  $C = 62.00$ ;  $H = 5.79$ .

0.1890 „ 0.2844 AgI.  $Et = 18.57$ .

$C_8H_{10}O_3$  requires  $C = 62.33$ ;  $H = 6.49$ ;  $Et = 18.83$  per cent.

### *Ellagic Acid.*

This yellow colouring matter is obtained from numerous tannin matters, as valonia, myrabolans, agarobilla, &c., being derived from the ellagitannic acid which is present in these substances. It can be prepared artificially by the action of alkalis on ethyl gallate (Ernst and Zwenger, *Annalen*, 1871, 159, 32), and is most probably a fluorene derivative. Owing to its sparing solubility in boiling alcohol,

it is not readily attacked by potassium acetate, and recourse was therefore had to its acetyl compound, which, although also sparingly soluble, is more suitable for the purpose. This substance,\* on digestion with boiling alcoholic potassium acetate, slowly becomes pale yellow without apparent solution, and to ensure complete conversion into the potassium salt it is necessary to heat for about four hours. The product was collected, washed with alcohol, and dried at  $160^{\circ}$ :

Found,  $K = 11.48, 10.98$ .  $C_{14}H_5O_8K$  requires  $K = 11.47$  per cent.

This compound consisted of minute, lemon-yellow needles, insoluble in cold alcohol. When submitted to the further action of boiling alcoholic potassium acetate for about two days, it is gradually transformed into a second salt without any appreciable change in its appearance:

Found,  $K = 20.19$ .  $C_{14}H_4O_8K_2$  requires  $K = 20.63$  per cent.

Thus obtained, the *dipotassium* salt of ellagic acid forms pale yellow, microscopic needles insoluble in alcohol.

By dissolving ellagic acid in sodium hydroxide solution and passing carbon dioxide through the liquid, Wöhler and Merklein (*Annalen*, 1845, 55, 129) obtained a salt,  $C_{14}H_4O_8Na_2, H_2O$ , and Ernst and Zwenger (*Annalen*, 1871, 159, 32) prepared the salt  $C_{14}H_5O_8Na, H_2O$  by the action of sodium carbonate on ethyl gallate.

### *Daphnetin.*

Daphnetin, a dihydroxycoumarin contained in the form of its glucoside, daphnin, in the bark of *Daphne alpina* and prepared synthetically (Pechmann, *Ber.*, 1884, 17, 1934) by the action of sulphuric acid on a mixture of pyrogallol and malic acid, is a moderately strong colouring matter, and gives the following shades with mordanted woollen cloth:

| Chromium.     | Aluminium.         | Tin.              | Iron.        |
|---------------|--------------------|-------------------|--------------|
| Olive-yellow. | Pale olive-yellow. | Very pale yellow. | Olive-black. |

Addition of potassium acetate to a boiling alcoholic solution of daphnetin caused the separation of a crystalline precipitate, which was collected, washed with alcohol, and dried at  $160^{\circ}$ :

Found,  $K = 14.03, 14.13, 14.10, 14.36$ .

$C_9H_6O_4, C_2H_5O_2K$  requires  $K = 14.13$  per cent.

\* According to Schiff (*Annalen*, 1873, 107, 79), acetyellagic acid is a yellow, crystalline powder, whereas the compound we obtained by means of acetic anhydride and sodium acetate crystallised in small, colourless needles. This point is consequently undergoing further investigation.

By decomposition with acid, it yielded 63.59 per cent. of daphnetin, whereas theory requires 64.49 per cent. It was obtained in the form of pale yellow needles, decomposed by boiling water with separation of daphnetin.

*Monopotassium Daphnetin*.—When alcoholic potash is added drop by drop to a boiling alcoholic solution of daphnetin, the orange-red coloration thus produced is not at first permanent, but quickly disappears. The pale yellow, crystalline precipitate formed at this stage was collected, washed with alcohol, and dried at 160°:

Found,  $K = 9.93$ .  $C_{18}H_{11}O_8K$  requires  $K = 9.90$  per cent.

It consisted of pale yellow, prismatic needles, soluble, with decomposition, in boiling water, from which crystals of daphnetin were deposited on cooling.

If the addition of alcoholic potash is continued until the orange-red coloration is permanent, a precipitate of minute, garnet-red, prismatic needles then separated:

Found,  $K = 18.07$ .  $C_9H_5O_4K$  requires  $K = 18.05$  per cent.

Monopotassium daphnetin is soluble in cold water, forming an orange-yellow liquid, which is not decomposed at the boiling point. The barium salt is obtained as a dull orange precipitate when barium chloride is added to this solution.

### *Flavone Group.*

In the previous communication (*loc. cit.*), it was pointed out that with the exception of morin those colouring matters of the flavone group which reacted with potassium acetate to form sparingly soluble monopotassium salts possessed two hydroxyl radicles in the ortho-position relatively to one another. The description in subsequent papers of the salts of gossypetin,  $C_{15}H_9O_8K$ , myricetin,  $C_{15}H_9O_8K$ , quercetagenin,  $C_{15}H_9O_8K$ , and luteolin,  $C_{15}H_9O_6K$ , was in harmony with this deduction, but on the other hand, kampherol, which gives the salt  $C_{15}H_9O_6K$ , proved a second exception to the rule. It was therefore desirable to examine in this respect the colouring matters kampheride (kampherol monomethyl ether) and galangin, and although the work has been hampered by the small amounts of these rare colouring matters available, the results have been sufficiently good for the present purpose.

*Monopotassium galangin* is usually obtained as a bright yellow, amorphous precipitate, but by employing a somewhat dilute solution and cautiously adding, the acetate is then deposited in minute needles:



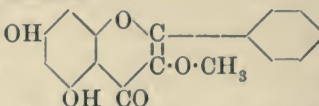
Found, K = 11.67, 11.67, 11.24 per cent.

$C_{15}H_9O_5K, H_2O$  requires K = 11.96 per cent.

*Monopotassium kampheride* is a bright yellow salt :

Found, K = 10.87.  $C_{16}H_{11}O_6K, H_2O$  requires K = 10.95 per cent.

In both cases, these salts are decomposed by boiling water with regeneration of the colouring matter.

*Galangin monomethyl ether*, , it will be

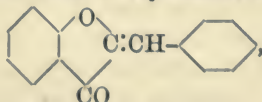
observed, is constituted, as regards the free hydroxyl groups which it contains, in an analogous manner to chrysin (*loc. cit.*). As was to be anticipated, therefore, it gave no sparingly soluble salt by this method.

It is worthy of mention that the above three colouring matters in the presence of acetic acid yield crystalline, yellow compounds with mineral acids which are readily decomposed by water. Galangin monomethyl ether, however, resembles rhamnetin (Trans., 1895, 67, 650) in this respect, for the sulphuric acid compound only could be produced, and this with difficulty.

In the former communication, the salt  $C_{32}H_{23}O_{14}K$  was prepared from rhamnetin\* by treating an alcoholic solution of this substance with potassium acetate. It has now been found that on decomposing acetylramnetin in alcoholic solution with potassium acetate, the salt  $C_{16}H_{11}O_7K$  is produced in the form of orange-yellow needles, which are readily decomposed by boiling water :

Found, K = 11.07.  $C_{16}H_{11}O_7K$  requires K = 11.01 per cent.

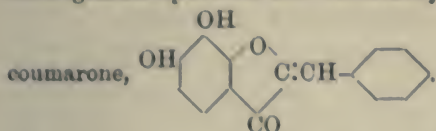
With the flavone derivatives at present examined containing contiguous hydroxyl groups, it may be noticed that in no case have these radicles been situated in the pheno- $\gamma$ -pyrone nucleus. Such compounds have not as yet been isolated from natural sources, and their preparation synthetically is somewhat difficult. A closely allied class of colouring matters derived from benzylidenecoumarone,



has been synthetically prepared by Friedländer and Rüdts (*Ber.*, 1896, 29, 878) by the interaction of *o*-hydroxyaromatic ketones which have been chlorinated in the side chain and aromatic aldehydes. Thus

\* Since the previous communication, the position of the methoxy-group in rhamnetin has been determined (Trans., 1902, 81, 469), and consequently the influence this was suggested to bear upon its salt-forming property requires modification.

chlorogallacetophenone and benzaldehyde yield dihydroxybenzylidene-

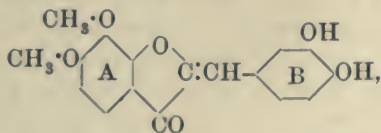


A concentrated alcoholic solution of this colouring matter, on treatment with alcoholic potassium acetate at the boiling point, at once deposited a salt crystallising in orange-yellow needles which were collected and washed with alcohol. Thus prepared, it appeared to contain alcohol of crystallisation, for on heating at  $100^{\circ}$  for two days it became orange-red and lost 11.54 per cent. in weight.

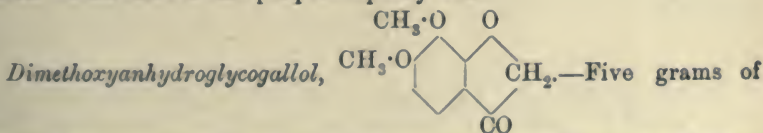
Found,  $K = 11.60$ .  $C_{15}H_{10}O_4 \cdot C_2H_3O_2K$  requires  $K = 11.08$  per cent.

It thus appeared to be a compound of the colouring matter with potassium acetate analogous to those given by daphnetin and hesperitin (*loc. cit.*). A monopotassium salt would require  $K = 13.37$  per cent., but even after drying at  $160^{\circ}$  for three days, which caused the substance to become dark coloured and probably partially decomposed, it then contained no more than 12.24 per cent. of potassium.

For the sake of comparison, it was now of interest to study a colouring matter of this group containing only two free hydrogen groups in the benzylidene nucleus, and in the ortho-position relatively to one another. Such a compound has already been prepared, but from the materials which were available it was more convenient to construct a colouring matter having the constitution



which would answer the purpose equally well.



chlorogallacetophenone dissolved in methyl alcohol were treated with excess of methyl iodide and the mixture digested at the boiling point during two days with a solution of 6 grams of potassium hydroxide in methyl alcohol added drop by drop. It is necessary that the alkali be added very gradually, otherwise the result is not satisfactory. That portion of the product insoluble in aqueous potassium hydroxide was purified by crystallisation from alcohol, from which it separated in long, glistening, pale yellow needles melting at  $122^{\circ}$ :

0.1101 gave 0.2495  $\text{CO}_2$  and 0.0518  $\text{H}_2\text{O}$ .  $\text{C} = 61.80$ ;  $\text{H} = 5.21$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 61.85$ ;  $\text{H} = 5.15$  per cent.

Molecular proportions of this substance and protocatechuic aldehyde were dissolved in boiling alcohol, a small quantity of aqueous hydrochloric acid was added, and the digestion continued for about half-an-hour. On addition of hot water and cooling, orange-red needles separated which were collected, washed with a little ether, and purified by crystallisation from dilute alcohol:

0.1138 gave 0.2712  $\text{CO}_2$  and 0.0463  $\text{H}_2\text{O}$ .  $\text{C} = 64.99$ ;  $\text{H} = 4.52$ .

$\text{C}_{17}\text{H}_{14}\text{O}_6$  requires  $\text{C} = 64.96$ ;  $\text{H} = 4.46$  per cent.

This colouring matter evidently has the constitution given above. When pure, it has an orange colour, and resembles in its reactions the colouring matters of this group, previously described by Friedländer (*loc. cit.*).

Addition of potassium acetate to its solution in boiling alcohol causes the production of a deep orange-red coloration, and, on cooling, the monopotassium salt separates in the form of a granular precipitate. This was collected and washed with cold alcohol, in which it is somewhat soluble:

Found,  $\text{K} = 11.16$ .  $\text{C}_{17}\text{H}_{13}\text{O}_6\text{K}$  requires  $\text{K} = 11.08$  per cent.

It is thus evident, as regards these colouring matters, that from the presence of contiguous hydroxyl groups in the nuclei A or B, the formation of a monopotassium salt in this manner can be anticipated, and it is reasonable to suppose that analogous compounds of the closely allied flavone group will possess a similar property. It is probable, however, that the position of these contiguous hydroxyl groups in the various nuclei may have an important bearing upon this reaction. Unfortunately, however, this point could not be elucidated, for no colouring matters of this description have hitherto been synthetically prepared.

#### *Carminic Acid.*

According to the latest researches, carminic acid, the colouring matter of cochineal, is probably a hydrindene derivative (Liebermann, *Ber.*, 1898, 31, 2079). Various salts of this substance have been described, and those obtained by Hlasiwetz and Grabowski (*Annalen*, 1867, 141, 335) are most worthy of mention. By means of alcoholic potash, these chemists obtained the salt  $\text{C}_{11}\text{H}_{10}\text{O}_7\text{K}$ , and from this the barium and calcium compounds were prepared by double decomposition.

The material employed by us was purchased from Kahlbaum; a portion was recrystallised, but this, it subsequently appeared, was unnecessary.



Hlasiwetz and Grabowski (*loc. cit.*) mention that when alcoholic potash is slowly added to an alcoholic solution of carminic acid a red precipitate is first formed, which changes to violet on the addition of more alkali. It was found that potassium acetate behaves similarly. The violet or purplish-coloured precipitate produced by employing excess of the reagent was collected on filter paper, washed several times with boiling alcohol, drained by means of the pump, and again washed two or three times with alcohol and dried at  $160^{\circ}$ :

Found, K = 14.26, 14.29.  $C_{11}H_{11}O_6K$  requires K = 14.03 per cent.

*Monopotassium carminate* is soluble in boiling water (with a violet-red coloration) without apparent decomposition, and resembles, in this respect, the corresponding salts of the anthraquinone colouring matters. The barium salt, prepared from this in the usual manner, is a violet-black powder almost insoluble in water:

Found, Ba = 21.50.  $C_{22}H_{22}O_{12}Ba$  requires Ba = 22.27 per cent.

Hlasiwetz and Grabowski's violet potassium salt was prepared according to their methods, and was evidently identical with that obtained by means of potassium acetate.

To obtain some insight into the composition of the red salt, a small quantity was prepared by adding the acetate drop by drop to a boiling alcoholic solution of carminic acid so long as the red precipitate thus produced showed no violet tinge. The product was collected, washed with boiling alcohol, and dried at  $160^{\circ}$ :

Found, K = 7.  $C_{22}H_{23}O_{12}K$  requires K = 7.52 per cent.

It formed a scarlet powder, almost indistinguishable from carminic acid itself, but was insoluble in cold alcohol, although dissolving easily in water to a red liquid. It is probably a monopotassium salt of a double molecule of carminic acid, but this is not certain, as the molecular weight of this colouring matter may possibly be represented as  $(C_{11}H_{12}O_6)_2$ .

A sodium salt,  $C_{22}H_{23}O_{12}Na$ , may be prepared in a similar manner to the potassium compound, and is a scarlet, amorphous powder:

Found, Na = 4.63.  $C_{22}H_{23}O_{12}Na$  requires Na = 4.58 per cent.

### *Styrogallol.*

This colouring matter is a dihydroxyanthracoumarin, and is prepared by heating a mixture of cinnamic and gallic acids with sulphuric acid. Owing to its sparing solubility in alcohol, it was converted into its diacetyl derivative, and this was digested with boiling alcoholic

potassium acetate for about two hours.\* The substance, without appearing to dissolve, was gradually converted into a purplish, crystalline mass which was collected, washed with alcohol, and dried at  $160^{\circ}$  :

Found,  $K = 12.56, 12.59$ .  $C_{16}H_7O_5K$  requires  $K = 12.26$  per cent.

*Monopotassium styrogallol* forms minute, purplish-coloured needles, and is soluble in boiling water with a red coloration.

### *Naphthazarin.*

On adding potassium acetate to a boiling alcoholic solution of pure crystallised naphthazarin, the deep red liquid gradually became of a brownish-yellow tint as if a reduction had ensued. On standing for a short time with access of air, the red colour was restored, and a finely divided, black precipitate was deposited. This was collected while still hot, washed repeatedly with boiling alcohol, then transferred to the filter pump, and again washed two or three times with alcohol and finally dried at  $160^{\circ}$  :

Found,  $K = 8.09, 8.20, 7.99$ .  $(C_{10}H_6O_4)_2 \cdot C_2H_3O_2K$  requires  $8.16$  per cent.

This substance is a purplish-black, amorphous powder, and is sparingly soluble in cold water, forming a purple solution.

### *Curcumin.*

As stated in the previous communication, curcumin, the colouring matter of turmeric, on solution in alcohol and treatment with potassium acetate, gives a blood-red coloration but no deposit. It has since been found that if this solution be evaporated, a semi-solid, orange-red mass, consisting of fine, hair-like needles, separates. This precipitate, which is somewhat soluble in alcohol, was collected, washed with small quantities of this solvent, and finally two or three times with ether. Numerous preparations of this substance were analysed, but although these gave results sufficiently accurate for the purpose, they did not accord perfectly either among themselves or with the latest molecular weight,  $C_{21}H_{20}O_6$ , assigned to this substance by Ciamician and Silber (*Ber.*, 1897, 30, 192). Dried at  $100^{\circ}$ , it gave :

$K = 10.07, 10.90, 9.72, 10.21$ .

$C_{21}H_{19}O_6K$  requires  $K = 9.60$  per cent.

This want of agreement may have been due to incomplete washing,

\* By the decomposition of the acetyl derivatives in this manner, ethyl acetate is formed, and the reaction appears to be as follows :



for the operation is somewhat difficult owing to the solubility of the substance in alcohol and its tendency to clot together. When dried at the ordinary temperature, this salt has an orange-brown colour, which at  $100^{\circ}$  changes to a maroon tint, and at  $160^{\circ}$  becomes darker and partially resinifies. Jackson and Menke (*Amer. Chem. J.*, 1883, 4, 77) describe a salt,  $C_{14}H_{13}O_4K$ .

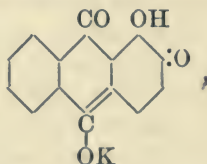
*Gallein*.—The commercial product was acetylated and the acetyl derivative, after purification, digested with a boiling alcoholic solution of potassium acetate for some hours. A potassium salt is thus obtained in the form of fine, maroon-coloured, prismatic needles possessing a green iridescence, but unfortunately its exact composition has not been determined. After drying at  $100^{\circ}$ , it slowly but steadily loses weight at  $160^{\circ}$ , and a further loss is experienced at  $180^{\circ}$  without apparent decomposition. For example, a specimen at  $100^{\circ}$  contained 13.8, at  $160^{\circ}$ , 16.7, and at  $180^{\circ}$ , 19.7 per cent. of potassium, and similar results were obtained from other preparations. A further study of this substance will be instituted.

#### *Summary.*

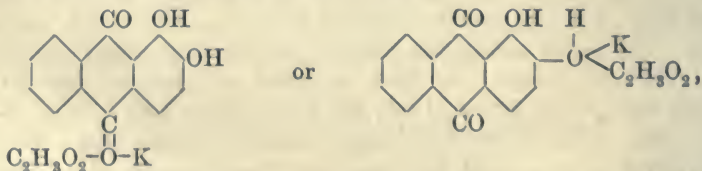
The results of this and the preceding investigation indicate that all phenolic colouring matters which possess strong tinctorial properties are capable of decomposing the alkali acetates in the way indicated, with formation of sparingly soluble salts. As a rule, mono-substituted salts are produced; but in some cases additive products of the colouring matter and alkali acetate result. The weaker dyes of this class, such as apigenin, chrysin, and vitexin, give no insoluble precipitate, but as their alcoholic solutions are coloured yellow by addition of the acetate, it appears likely that some unstable compound is thus formed. It was previously suggested that the formation of the mono-substituted salts might be explained according to the quinonoid theory of coloured compounds, and we are at present inclined to retain this view. An interesting point which was referred to in the previous paper, and which has now been accentuated by further work, was the fact that, in the flavone series, the compounds which gave these salts gave also some well-defined additive products with mineral acids. The latter substances, hitherto formulated only according to the quinonoid theory, are now regarded as oxonium derivatives (Collie and Tickle, *Trans.*, 1899, 75, 714; Baeyer and Villiger, *Ber.*, 1901, 34, 2679). The "acid" and "basic" natures of the flavone derivatives as expressed by these two reactions are so markedly similar in each case as to suggest an intimate connection, and a likelihood that both, at least in the first instance, are due to the same cause. Certain compounds have been isolated which are additive



products of the colouring matter with potassium acetate; a compound of morin with potassium oxalate has also been referred to, and no doubt it would be possible to prepare numerous salts of this type. These substances are isolated when the phenol, although forming mono-substituted salts in the presence of alcoholic potassium or sodium hydroxide, is not sufficiently acidic to decompose the potassium acetate or other salt. Accordingly, it is therefore considered probable that in all cases the first step in this reaction is the production of an additive product of the colouring matter and the alkali salt; this, as a rule, is too unstable for isolation, and is rapidly decomposed with formation of the mono-substituted salt. Again, when the alkali hydroxide is employed at first, an additive compound is possibly formed, which changes almost immediately into the salt derived from the acetate. Such additive products can, of course, be readily formulated as oxonium derivatives,  $K-O-C_2H_3O_2$  or  $K-O-OH$ , and this at once expresses their relation to the acid compounds, which is so marked in the flavone series. Assuming this to be correct, the question arises as to how the decomposition of these unstable derivatives with subsequent formation of the mono-substituted salt is best explained. It has been pointed out that the potassium salt of alizarin on digestion with methyl iodide at  $220^\circ$  is converted into the monomethyl ether ( $OH : O \cdot CH_3 = 1 : 2$ ), and that the salts of other anthraquinone colouring matters behave similarly. Consequently, it was suggested that the constitution of the potassium salt was best represented as:



the marked change of colour between this substance and alizarin itself being due to an alteration in the quinonoid form. In accordance with this, therefore, the unstable additive compound of alizarin with the acetate could be formulated in two ways:




the first of which might be considered preferable, as it more readily expresses the change to the monopotassium salt as represented.

The fact has been noted that certain mono-substituted salts as, for

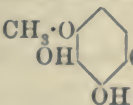
instance, those of alizarin and gallacetophenone, are stable towards boiling water, whereas those of the flavone series are not. This distinction suggested the possibility that the flavone compounds were not true salts, but might be represented as additive compounds of the colouring matter and alkali hydroxide. From the previous work, this did not appear likely, but to set all doubt at rest the potassium derivative of morin was again investigated, with the result that this must be regarded as a true salt,  $C_{15}H_9O_7K$ , and not an additive compound,  $C_{15}H_{10}O_7 \cdot KHO$  (found  $K = 11.45, 11.46$ ; calc.  $K = 11.47$ ).

As an explanation of the instability of the flavone (and other) salts, it is suggested that in the presence of water monopotassium quercetin, for example, tends to pass into the oxonium derivative,  $C_{15}H_{10}O_7 \cdot KHO$ , which being unstable is decomposed into quercetin and its salt,  $C_{15}H_9O_7K$ .

In support of the quinonoid structure of the salts, it is interesting to note that all the colouring matters of known constitution at present examined can readily be represented as *p*-quinonoid compounds. Except in the case of flavone derivatives (Trans., 1902, 81, 590), it appears to be generally true that all colouring matters carefully investigated, from this point of view, contain two hydroxyl groups in the ortho-position relatively to one another. As this peculiar salt formation may be taken as an expression of the dyeing property, it would be most interesting to determine whether an

acetyl catechol having the constitution  $OH$    $CO \cdot CH_3$  would be a

dyestuff, as this could evidently not be expressed as a *p*-quinonoid compound. Unfortunately, this and similarly constituted substances do not seem to have been prepared, although it is considered probable that the gallacetophenone monomethyl ether described in this paper

has the constitution  $CH_3 \cdot O$    $CO \cdot CH_3$ . Definite knowledge of the

behaviour of such phenolic compounds should decide the constitution assigned to these salts.

The tendency of some colouring matters to form what may be termed *semimonosubstituted salts*, as in the case of daphnetin,  $C_9H_6O_4 \cdot C_9H_5O_4K$ , is interesting and has led us to attempt the formation of such compounds from alizarin and other colouring matters, but as yet without success. It is evident that these substances, as in the case of the product obtained from daphnetin and potassium acetate, &c., could be represented as oxonium derivatives in the manner suggested above, but the peculiar gallacetophenone com-

pound,  $(C_8H_8O_4)_2 \cdot C_8H_7O_4K$ , indicates that such an explanation is hardly feasible. The existence of these semi-monosubstituted salts indicates that the composition of such derivatives must not without further evidence be taken to represent the molecular weight of the compound under consideration; as has been the case with hesperitin and rottlerin (Trans., 1898, 73, 1035; 1895, 67, 230). The former yielded derivatives,  $C_{32}H_{28}O_{12} \cdot C_2H_3O_2K$  and  $C_{32}H_{27}O_{12}K$ , and the latter  $C_{33}H_{29}O_9K$  and  $C_{33}H_{29}O_9Na$ , and other methods of molecular weight determination will be carried out to determine if these substances are semi-salts or otherwise.

It has been observed in the cases of ellagic acid and galloflavin that by means of potassium acetate both colouring matters form dipotassium salts. This apparently abnormal behaviour appears to be due to the fact that both substances are acids, and that to the carboxylic group is due the presence of the second potassium atom in these compounds. The special activity of one hydroxyl group in colouring matters known to possess several such radicles is no doubt of importance in connection with their property of forming lakes with the heavier metals and their basic salts. It would be extremely interesting if the corresponding mono-substituted salts of aluminium and tin could be prepared in order to observe the colour of these products, and to determine how closely they resemble the shades produced in the ordinary manner with mordanted fabrics. Compounds, however, of this simple character are not produced by methods of soluble decomposition, and salts of a basic nature have only at present been isolated when experimenting in this direction.

In connection with oxonium derivatives, it may be here mentioned that during experiments with kampherol, with the object of preparing Testoni's methylkampherol trimethyl ether (*Gazzetta*, 1900, 30, ii, 327), a substance resembling but not identical with this compound resulted. It melted at  $182-185^\circ$ , and although analyses were carried out, these, as was subsequently discovered, were vitiated by the fact that the product contained a considerable quantity of iodine. Owing to the scarcity of the material and the expense of the methods necessary for isolating kampherol, these experiments have not as yet been repeated, but it is possible that the compound in question may be represented as an oxonium derivative containing the group  $Me-\overset{\overset{O}{\parallel}}{O}-I$ , analogous to the substance,  $C_7H_8O_3 \cdot EtOH$ , which Collie and Steele (Trans., 1900, 77, 971) obtained from dimethylpyrone. The subject will be further investigated.



## XII.—Interactions of Ketones and Aldehydes with Acid Chlorides—the Formation of Benzoxyolefines and 1-Benzoxycamphene.

By FREDERICK HERBERT LEES.

IN the course of an investigation on the constituents of an essential oil of rue (Power and Lees, *Trans.*, 1902, 81, 1585), a mixture was isolated consisting of methyl heptyl and methyl nonyl ketones, together with methylheptyl- and methylnonyl-carbinols. To separate the two classes of substances, the mixture was boiled with an excess of benzoyl chloride in order to convert the alcohols into benzoic esters, as it was hoped that subsequent fractional distillation in a vacuum would achieve the object. Although sufficient benzoyl chloride was employed to convert the whole of the oil into ester had it consisted entirely of methylheptylcarbinol, it was observed on distillation of the product that very little of the chloride remained, and that not only had the alcohols been converted into esters, but the ketones in some manner had also formed substances of considerably higher boiling point.

Although the primary object of this experiment was not thus attained, and the separation was subsequently carried out in an entirely different way (*loc. cit.*), it appeared of interest to examine the substances formed by the interaction of the ketones mentioned and benzoyl chloride.

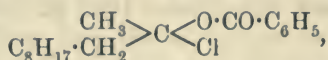
Methyl *n*-nonyl ketone and benzoyl chloride readily interact, with elimination of hydrogen chloride, when a mixture in molecular proportion is boiled for some hours. The condensation product is an oil of high boiling point and has the formula  $C_{18}H_{26}O_2$ ; its formation may be represented by the equation :



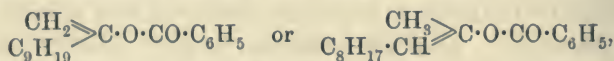
With regard to the constitution of this compound, the question at issue was whether the benzoyl radicle was attached to carbon or to oxygen, or, in other words, whether the substance was a diketone or a benzoxyolefine. The substance was insoluble in aqueous potassium hydroxide, and its alcoholic solution did not develop a coloration on the addition of ferric chloride, facts which excluded the possibility of its being either a  $\beta$ -diketone or an enolic modification of the latter. Moreover, as the compound was readily hydrolysed by warm dilute alcoholic potassium hydroxide with separation of potassium benzoate, and by hydroxylamine under the same conditions with the formation of methylnonylketoxime, it was evident that the benzoyl radicle was in

combination with oxygen, and that the substance was a benzoxy-olefine. This view of its constitution was further supported by the fact that by treatment with bromine a dibromide was formed.

The formation of an acyloxy-derivative of an olefine by interaction of a mono-oxygenated ketone with an acid chloride has not hitherto been observed. The most probable explanation of the reaction is that in the first instance the benzoyl chloride becomes attached to the carbonyl group of the ketone, forming the intermediate compound :

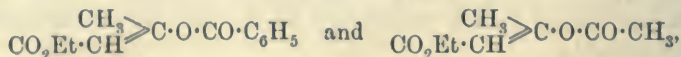


which, by loss of hydrogen chloride, would give rise to a compound having one or other of the two following formulæ :

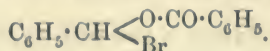


It has not yet been ascertained which of the two expressions represents the substance  $\text{C}_{18}\text{H}_{26}\text{O}_2$ , and so it is provisionally designated *β-benzoxyundecylene*.

The above explanation of the reaction receives support from the fact that Claisen and Haase (*Ber.*, 1900, 33, 1242), in continuation of the researches of the former on substances containing the grouping  $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ , have prepared ethyl O-benzoylacetoacetate and ethyl O-acetylacetoacetate of the respective formulæ :



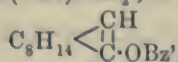
by the interaction of ethyl acetoacetate with the acid chlorides in presence of pyridine, and trace the course of the reaction on the plan given above for the formation of *β-benzoxyundecylene*. In justification of their scheme, Claisen and Haase refer to an observation of Claisen's (*Ber.*, 1881, 14, 2475) that benzaldehyde readily forms an additive compound, with benzoyl bromide, of the constitution



The reaction employed in the production of *β-benzoxyundecylene* has been extended to other mono-oxygenated ketones and a mono-oxygenated aldehyde; the behaviour of a ketone with aliphatic acid chlorides was also studied. The results of these investigations and the substances obtained are as follows.

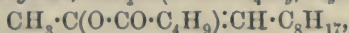
Neither acetone nor methyl *n*-propyl ketone interacted with benzoyl chloride. On the other hand, from methyl *n*-butyl ketone, methyl *sec.*-hexyl ketone, methyl *n*-heptyl ketone, acetophenone, camphor, and heptaldehyde, there were respectively prepared: *β-benzoxyhexylene*,

$\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{C}_4\text{H}_9$  or  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CH}\cdot\text{C}_3\text{H}_7$ ;  $\beta$ -benzoxy- $\gamma$ -methylheptylene,  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CHMe}\cdot\text{C}_4\text{H}_9$  or  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CMe}\cdot\text{C}_4\text{H}_9$ ;  $\beta$ -benzoxy-nonylene,  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{C}_7\text{H}_{15}$  or  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CH}\cdot\text{C}_6\text{H}_{13}$ ;  $\alpha$ -benzoxy- $\alpha$ -phenylethylene,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{OBz})\cdot\text{CH}_2$ ; 1-benzoxycamphene,



and  $\alpha$ -benzoxy- $\alpha$ -heptylene,  $\text{C}_5\text{H}_{11}\cdot\text{CH}\cdot\text{CH}\cdot\text{OBz}$ .

Methyl *n*-nonyl ketone did not interact with acetyl chloride when the mixture was boiled for several hours; with valeryl chloride, however,  $\beta$ -valeroxyundecylene,  $\text{CH}_3\cdot\text{C}(\text{O}\cdot\text{CO}\cdot\text{C}_4\text{H}_9)\cdot\text{C}_9\text{H}_{19}$  or



resulted.

The fact that acetone and methyl *n*-propyl ketone does not interact with benzoyl chloride or methyl *n*-nonyl ketone with acetyl chloride is probably owing to the temperatures at which the respective mixtures boiled not being sufficiently high. On the other hand, it might be possible to effect condensation even in these cases if a tertiary base were employed as a condensing medium (compare Claisen and Haase, *loc. cit.*).

The substances described in this paper are represented as esters of the enolic form of the respective carbonyl compounds from which they are derived, or, in other words, they are esters of that class of alcohols of which the hypothetical vinyl alcohol,  $\text{CH}_2\cdot\text{CH}\cdot\text{OH}$ , is the simplest member. This class may be generally represented by the types



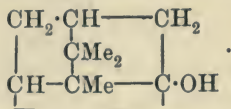
With regard to substances of these types, Erlenmeyer (*Ber.*, 1880, 13, 309; 1881, 14, 320) has stated that they are incapable of free existence, and that when, by certain reactions, they might be expected to result, the isomeric ketonic or aldehydic form, as the case may be, is produced instead. This generalisation has always held good for mono-oxygenated substances of the above types, and the only exceptions are amongst those substances which contain one or more negative oxygenated complexes attached to the carbon atom adjacent to that associated with the critical oxygen atom.

The substances described in this paper conform to Erlenmeyer's rule, and by its means the formation of methylnonylketoxime by the interaction of  $\beta$ -benzoxyundecylene with hydroxylamine is readily explained.

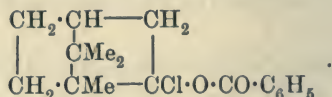
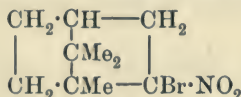
The formation of these acyloxy-olefines and of 1-benzoxycamphene would appear to represent the first instance of the direct transformation of a mono-oxygenated carbonyl compound into a derivative of its enolic form. With regard to benzoxycamphene, however, some doubt existed as to its being correctly represented by the



formula  $C_8H_{14} \begin{smallmatrix} \text{CH} \\ \diagup \text{C} \cdot \text{OBz} \end{smallmatrix}$ , and this arose from a consideration of Forster's work on a hydroxycamphene (Trans., 1901, 79, 644; 1902, 81, 264), to which he assigns the highly probable constitution



This substance was produced by direct steps from 1:1-bromonitrocamphane, and Forster pointed out that the origin of the uncertainty in fixing its constitution lies in the several possibilities for the elimination of hydrogen bromide from the former compound. That an uncertainty dependent on an analogous reason can exist with regard to benzoxycamphene is apparent if the structures of 1:1-bromonitrocamphane and 1:1-chlorobenzoxycamphane—the additive compound of camphor and benzoyl chloride which is assumed to be formed in the production of benzoxycamphene—are placed side by side:



The question to be decided was whether benzoxycamphene might not possess a structure similar to that of hydroxycamphene.

Hydroxycamphene is stable in presence of alkalis, and does not react with hydroxylamine (Forster, *loc. cit.*), a behaviour which accords with its constitution, whereby a transformation into camphor would, in the first instance, involve the disruption of a trimethylene ring of

the type  $\begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CH} \text{---} \text{C} \cdot \text{OH} \end{array}$ . Such a change is hardly likely to occur under

the influence of the agents mentioned. Benzoxycamphene, on the other hand, is hydrolysed by alkalis or hydroxylamine, yielding, however, not a hydroxycamphene stable to these reagents, but camphor and camphoroxime respectively; benzoxycamphene, therefore, on hydrolysis gives a hydroxycamphene conforming to Erlenmeyer's rule, which includes those substances of the type  $>\text{C}:\text{C}(\text{OH})-$ ; moreover, Forster has shown that hydroxycamphene, on treatment with bromine with subsequent elimination of hydrogen bromide, affords a bromocamphor which melts at  $78^\circ$ , has  $[\alpha]_D +19^\circ$ , and is certainly not an  $\alpha$ -bromo-derivative. Benzoxycamphene, however, on treatment with bromine followed by elimination of benzoyl bromide, gave a bromocamphor which melted at  $76^\circ$ , had  $[\alpha]_D +131^\circ$ , and was in all respects identical with  $\alpha$ -bromocamphor,  $C_8H_{14} \begin{smallmatrix} \text{CHBr} \\ \diagup \text{C} \text{---} \text{CO} \end{smallmatrix}$ .

The evidence thus adduced affords conclusive proof of the correctness of the structure assigned to 1-benzoxycamphene, and of the view that it is the benzoate of enolic camphor.

### EXPERIMENTAL.

In the preparation of the substances described in this paper, the ketone or aldehyde and the acid chloride, in molecular proportion, were boiled together in a reflux apparatus for 4—6 hours, and the interaction was accompanied by a copious evolution of hydrogen chloride. The isolation of the condensation product was effected by direct fractional distillation, except in the case of the substance obtained from the aldehyde. The properties of  $\beta$ -benzoxundecylene resemble those of the other benzoxo-derivatives described in this paper, and one description will therefore suffice for the group.

*$\beta$ -Benzoxundecylene*,  $\text{CH}_2\cdot\text{C}(\text{OBz})\cdot\text{C}_9\text{H}_{19}$  or  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CH}\cdot\text{C}_8\text{H}_{17}$ .

This was prepared from methyl *n*-nonyl ketone and benzoyl chloride. Fractional distillation of the product under 50 mm. pressure resulted in the separation of a quantity of unchanged material boiling below  $140^\circ$  (50 mm.), from the condensation product which distilled at  $230$ — $240^\circ$ . On redistillation, the latter passed over at  $233$ — $235^\circ$  (50 mm.) as a light yellow oil, and the yield amounted to 100 per cent. of the methyl nonyl ketone employed. On analysis:

0.0941 gave 0.2696  $\text{CO}_2$  and 0.0788  $\text{H}_2\text{O}$ .  $\text{C} = 78.1$ ;  $\text{H} = 9.3$ .

$\text{C}_{18}\text{H}_{26}\text{O}_2$  requires  $\text{C} = 78.8$ ;  $\text{H} = 9.5$  per cent.

2.1095 depressed the freezing point of 21.75 grams of phenol by  $1.135^\circ$ , whence mol. wt. = 281.  $\text{C}_{18}\text{H}_{26}\text{O}_2 = 274$ .

0.9624 required NaOH equivalent to 36 c.c. of a decinormal solution, instead of 35.1 c.c., the calculated amount.

$\beta$ -Benzoxundecylene is insoluble in aqueous alkali hydroxides and its alcoholic solution gives no coloration with ferric chloride. Its solution in dry carbon disulphide or chloroform, cooled below  $0^\circ$ , instantaneously decolorises bromine, and its cold alcoholic solution reduces potassium permanganate.  $\beta$ -Benzoxundecylene is immediately hydrolysed by warm dilute alcoholic potash with separation of potassium benzoate.

*Action of Hydroxylamine.*—Sodium (3.31 grams) dissolved in absolute alcohol (50 c.c.) was added to a solution of hydroxylamine hydrochloride (10 grams) in water (20 c.c.);  $\beta$ -benzoxundecylene (10 grams) dissolved in alcohol (20 c.c.) was then introduced, and the

mixture boiled for 6 hours. After removing some of the alcohol, water was added and the liquid extracted with ether, the ethereal solution was washed first with water and then with dilute sodium carbonate solution to remove benzoic acid; it was then dried with anhydrous potassium carbonate and the ether removed. The product was an oil which soon formed a crystalline paste; this was drained on a porous tile and the dry, crystalline substance recrystallised from dilute alcohol, from which it separated as long needles melting at  $46^{\circ}$ . On analysis:

0.1062 gave 0.2788  $\text{CO}_2$  and 0.1206  $\text{H}_2\text{O}$ .  $\text{C} = 71.6$ ;  $\text{H} = 12.6$ .

$\text{C}_{11}\text{H}_{23}\text{ON}$  requires  $\text{C} = 71.4$ ;  $\text{H} = 12.4$  per cent.

This substance is therefore methylonylketoxime, which melts at  $46^{\circ}$ .

The aqueous solution, from which the oxime had been extracted by ether, when acidified with sulphuric acid and warmed for some time on the water-bath, gave, on cooling, a quantity of benzoic acid.

*Action of Bromine.*—To a solution of  $\beta$ -benzoxyundecylene (10 grams) in dry carbon disulphide (20 c.c.) at  $0^{\circ}$ , dry bromine (6 grams), also dissolved in dry carbon disulphide (20 c.c.), was slowly added in the dark. The bromine was instantly absorbed without any formation of hydrogen bromide, and as soon as the whole had been decolorised the carbon disulphide was removed in a current of dry air. The product was a thick, light yellow oil and weighed 16 grams. In order to remove the last traces of carbon disulphide prior to analysis, a small portion was allowed to remain in a vacuum over solid paraffin for some time. On opening the desiccator, it was observed that the substance showed a tendency to lose hydrogen bromide; it was therefore analysed without delay:

0.3608 gave 0.273 AgBr.  $\text{Br} = 32.2$ .

$\text{C}_{18}\text{H}_{26}\text{O}_2\text{Br}_2$  requires  $\text{Br} = 37.0$  per cent.

It is thus seen that  $\beta$ -benzoxyundecylene forms a dibromide, which, however, is somewhat unstable.

*Action of Heat on the Dibromide.*—The dibromide was distilled under 50 mm. pressure; decomposition rapidly ensued, and fractions boiling below  $170^{\circ}$  and at  $170$ — $190^{\circ}$  were collected.

The former, on redistillation under the ordinary pressure, came over at  $220$ — $230^{\circ}$  as a heavy, strongly fuming liquid. When mixed with alcohol, much heat was developed, and when boiled with water it slowly dissolved, forming a clear solution, from which a quantity of benzoic acid separated on cooling. This fraction would thus seem to be benzoyl bromide.

The fraction which distilled at  $170$ — $190^{\circ}$ , on redistillation under



50 mm. pressure, gave a colourless oil which contained bromine in quantity, but did not fume. The amount available did not admit of further purification. Taking into consideration the constitution of  $\beta$ -benzoxyundecylene and the character of the substances formed by decomposition of 1-benzoxycamphene dibromide (p. 153), the product was in all probability a bromo-derivative of methyl nonyl ketone,  $C_{11}H_{21}OBr$ , containing the bromine atom attached to one or other of the carbon atoms adjacent to the carbonyl group. The determination of the exact position of this bromine atom would decide between the two possibilities for the constitution of  $\beta$ -benzoxyundecylene (compare p. 146).

*$\beta$ -Benzoxyundecylene*,  $CH_2:C(OBz) \cdot C_7H_{15}$  or  $CH_3 \cdot C(OBz) : C \cdot HC_6H_{13}$ .

This was prepared from methyl *n*-heptyl ketone and benzoyl chloride and the yield amounted to somewhat more than 100 per cent. of the ketone employed. It boils at  $210-211^\circ$  under 50 mm. pressure. On analysis:

0.1251 gave 0.3555  $CO_2$  and 0.1000  $H_2O$ .  $C = 77.5$ ;  $H = 8.9$ .

$C_{16}H_{22}O_2$  requires  $C = 78.0$ ;  $H = 8.9$  per cent.

2.062 required NaOH equivalent to 8.6 c.c. of a normal solution, instead of 8.4 c.c., the calculated amount.

*$\beta$ -Benzoxy- $\gamma$ -methylheptylene*,

$CH_2:C(OBz) \cdot CH(CH_3) \cdot C_4H_9$  or  $CH_3 \cdot C(OBz) : C(CH_3) \cdot C_4H_9$ .

This was prepared from methyl *sec*-hexyl ketone and benzoyl chloride and the yield amounted to 100 per cent. of the ketone employed. It boils at  $197-200^\circ$  under 50 mm. pressure. On analysis:

0.1163 gave 0.3288  $CO_2$  and 0.0896  $H_2O$ .  $C = 77.1$ ;  $H = 8.6$ .

$C_{15}H_{20}O_2$  requires  $C = 77.6$ ;  $H = 8.6$  per cent.

1.947 required NaOH equivalent to 8.6 c.c. of a normal solution, instead of 8.4 c.c., the calculated amount.

*$\beta$ -Benzoxyhexylene*,  $CH_2:C(OBz) \cdot C_4H_9$  or  $CH_3 \cdot C(OBz) : CH \cdot C_3H_7$ .

This was prepared from methyl *n*-butyl ketone and benzoyl chloride. The yield of condensation product was small as compared with that of the higher homologues, but a further amount was obtained by boiling the mixture of unchanged ketone and benzoyl chloride, separated from the higher boiling condensation product, for a further 4 hours. In this way, 13 grams of  $\beta$ -benzoxyhexylene boiling at  $170-175^\circ$  under 50 mm. pressure were obtained from 19 grams of ketone:

0.0932 gave 0.2591  $\text{CO}_2$  and 0.0665  $\text{H}_2\text{O}$ .  $\text{C} = 75.8$ ;  $\text{H} = 7.9$ .

$\text{C}_{13}\text{H}_{16}\text{O}_2$  requires  $\text{C} = 76.5$ ;  $\text{H} = 7.8$  per cent.

1.919 required  $\text{NaOH}$  equivalent to 9.7 c.c. of a normal solution, instead of 9.4 c.c., the calculated amount.

*a*-Benzoxo-*a*-phenylethylene,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{OBz}) \cdot \text{CH}_2$ .

This was prepared from acetophenone and benzoyl chloride, and the yield amounted to 80 per cent. of the ketone employed. It boils at  $229-230^\circ$  under 50 mm. pressure. On analysis:

0.1059 gave 0.3097  $\text{CO}_2$  and 0.0515  $\text{H}_2\text{O}$ .  $\text{C} = 79.8$ ;  $\text{H} = 5.4$ .

$\text{C}_{15}\text{H}_{12}\text{O}_2$  requires  $\text{C} = 80.3$ ;  $\text{H} = 5.4$  per cent.

0.8594 required  $\text{NaOH}$  equivalent to 38.8 c.c. of a decinormal solution, instead of 38.4 c.c., the calculated amount.

1-Benzoxycamphene,  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH} \\ \diagup \\ \text{C} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \end{smallmatrix}$ .

Camphor (50 grams) was dissolved in benzoyl chloride (50 grams) and the solution vigorously boiled for 6 hours. The product, when fractionated, yielded first a considerable proportion of unchanged material, and then, at a much higher temperature, a small amount (6 grams) of a nearly colourless oil which distilled at  $210-220^\circ$  under 50 mm. pressure. This operation was repeated several times, and in this way a considerable quantity of the oil was obtained; this substance, when redistilled, boiled at  $215-220^\circ$  under 50 mm. pressure. Benzoxycamphene is slightly laevorotatory, having  $\alpha_D - 1.5'$  in a 25 mm. tube. On analysis:

0.1202 gave 0.3477  $\text{CO}_2$  and 0.0844  $\text{H}_2\text{O}$ .  $\text{C} = 78.9$ ;  $\text{H} = 7.8$ .

0.0986 „ 0.2850  $\text{CO}_2$  „ 0.0704  $\text{H}_2\text{O}$ .  $\text{C} = 78.8$ ;  $\text{H} = 7.9$ .

$\text{C}_{17}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 79.7$ ;  $\text{H} = 7.8$  per cent.

0.8869 depressed the freezing point of 23 grams of phenol by  $1.058^\circ$ , whence mol. wt. = 269.  $\text{C}_{17}\text{H}_{20}\text{O}_2 = 256$ .

2.018 required  $\text{NaOH}$  equivalent to 7.85 c.c. of a normal solution, instead of 7.9 c.c., the calculated amount.

*Hydrolysis by Alcoholic Potassium Hydroxide.*—An alcoholic solution of 1-benzoxycamphene (10 grams) and potassium hydroxide (3 grams), when boiled for 45 minutes, yielded a mixture of camphor (6 grams) and potassium benzoate. The former was identified by its specific rotation,  $[\alpha]_D + 38.5^\circ$ , and by its oxime, which melted at  $118^\circ$ .

*Action of Hydroxylamine.*—This reagent was employed in alcoholic solution in the manner described under  $\beta$ -benzoxundecylene. The final products were benzoic acid and camphoroxime, the latter being

identified by its melting point,  $115-116^{\circ}$ , and its specific rotation,  $[\alpha]_D -42.1^{\circ}$ .

*Action of Bromine.*—1-Benzoxycamphene, when subjected to the action of bromine in the manner indicated under  $\beta$ -benzoxundecylene, afforded a heavy, yellow oil, which, when distilled under 30 mm. pressure, yielded two fractions, one distilling below  $150^{\circ}$  and the other at  $150-170^{\circ}$ . The first fraction, when redistilled under the ordinary pressure, boiled at  $220-230^{\circ}$  and was identified as benzoyl bromide. The higher fraction, which solidified after some hours, was drained on a porous tile and recrystallised several times from light petroleum; it separated in needles melting at  $75-76^{\circ}$ , and was identified as a bromocamphor.

This compound was also produced when 1-benzoxycamphene (2 grams), dissolved in cold glacial acetic acid (50 c.c.) containing several grams of anhydrous potassium acetate in solution, was slowly treated with bromine, added drop by drop, until present in slight excess. The product, when poured into water containing sulphurous acid, yielded a heavy oil, which subsequently crystallised on shaking with warm dilute sodium carbonate solution. This substance, when recrystallised from methyl alcohol, melted sharply at  $75-76^{\circ}$  and did not depress the melting point of  $\alpha$ -bromocamphor. That it was  $\alpha$ -bromocamphor was further shown by a determination of its specific rotation in ethyl alcohol, which proved to be  $[\alpha]_D +131^{\circ}$ .

*$\alpha$ -Benzoxy- $\alpha$ -heptylene,  $C_5H_{11} \cdot CH:CH \cdot O \cdot CO \cdot C_6H_5$ .*

This was prepared from *n*-heptaldehyde and benzoyl chloride. In this operation, large quantities of benzoic acid are produced, and on this account the product is conveniently purified by agitation with sodium carbonate solution in the presence of ether. The dried ethereal extract yielded two fractions, one boiling at  $190-200^{\circ}$  and the other at  $205-275^{\circ}$ , under 50 mm. pressure. The lower fraction, on redistillation, passed over almost entirely at  $195^{\circ}$  under 50 mm. pressure. On analysis:

0.1162 gave 0.3262  $CO_2$  and 0.0900  $H_2O$ .  $C=76.6$ ;  $H=8.6$ .

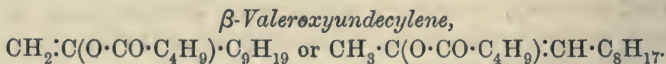
$C_{14}H_{18}O_2$  requires  $C=77.1$ ;  $H=8.3$  per cent.

This fraction, which consists therefore of  $\alpha$ -benzoxy- $\alpha$ -heptylene, resembles in all respects the benzoxy-derivatives prepared from the ketones. The yield amounted to 50 per cent. of the aldehyde employed.

The higher fraction, which distilled at  $205-275^{\circ}$  under 50 mm. pressure, doubtless consisted of condensation products of *n*-heptaldehyde (compare Perkin, Trans., 1883, 43, 45). The formation of a large amount of benzoic acid, which occurs in the preparation of



$\alpha$ -benzoxy- $\alpha$ -heptylene but not in the other condensations described in this paper, is explained by the fact that these condensations of  $n$ -heptaldehyde are accompanied by an elimination of water.



This was prepared from methyl  $n$ -nonyl ketone and valeryl chloride, and the yield amounted to 80 per cent. of the ketone employed. It boils at  $185\text{--}190^\circ$  under 50 mm., has a valerian-like odour, and closely resembles  $\beta$ -benzoxyundecylene in its properties. On analysis:

0.1009 gave 0.2795  $\text{CO}_2$  and 0.1081  $\text{H}_2\text{O}$ .  $\text{C}=75.5$ ;  $\text{H}=11.9$ .

$\text{C}_{16}\text{H}_{30}\text{O}_2$  requires  $\text{C}=75.6$ ;  $\text{H}=11.8$  per cent.

1.737 required  $\text{NaOH}$  equivalent to 6.9 c.c. of a normal solution, instead of 6.8 c.c., the calculated amount.

In the course of this investigation, I have received some valuable assistance from Mr. F. Shedden, and I take this opportunity of expressing my indebtedness to him.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

### XIII.—*Nitrotartaric Acid and some of its Ethereal Salts.*

By PERCY FARADAY FRANKLAND, HENRY LEONARD HEATHCOTE, B.Sc.,  
and HILDA JANE HARTLE, B.Sc.

ALTHOUGH the nitrates of tartaric acid and of its ethyl ester have formed the subject of several investigations, practically nothing is known of their optical properties.

Dinitrotartaric acid, or tartaric acid dinitrate, was probably first obtained by Reinsch (*Jahrb.*, 1849, 329) by dissolving tartaric acid in five times its weight of fuming nitric acid (sp. gr. 1.42). It was subsequently more completely studied, and first described as nitrotartaric acid by Dessaignes (*Jahrb.*, 1852, 475), who dissolved tartaric acid in 4.5 times its weight of strong nitric acid and then added an equal volume of strong sulphuric acid. By the spontaneous decom-

position of nitrotartaric acid, Dessaignes obtained oxalic and tartronic acids (*Jahrb.*, 1854, 396). He similarly prepared nitroracemic acid (*Jahrb.*, 1857, 306), from which tartronic acid was also obtained by spontaneous decomposition. By the action of ammonium sulphide on nitrotartaric acid, Dessaignes obtained tartaric acid, whilst by the action of sulphuretted hydrogen on ammonium nitroracemate, racemic acid was obtained. Dessaignes further mentions that, whilst nitroracemic acid is inactive, Chautard had shown that nitrotartaric acid was active to polarised light. This is the only reference to the optical activity of nitrotartaric acid or any of its derivatives that we have been able to find in the literature of the subject.

The decomposition of nitrotartaric acid has been further investigated by Demole (*Ber.*, 1877, 10, 1788), who found that by boiling the acid with dilute alcohol (sp. gr. 0.925) tartronic acid is almost exclusively obtained, traces of oxalic acid being formed only occasionally.

Dinitrotartaric acid was also employed by Kekulé (*Annalen*, 1883, 221, 244) for the preparation of dihydroxytartaric acid, which he showed to be identical with what was previously known as carboxytartronic acid, and which he obtained by retarding the decomposition of dinitrotartaric acid by adding to its solution in ether some ethyl nitrite and leaving the mixture at the ordinary temperature of the air.

The only known ethereal salt of dinitrotartaric acid was prepared by Henry (*Ber.*, 1870, 3, 530), who describes the diethyl ester as a viscid oil which solidifies on standing, and which, on recrystallisation by spontaneous evaporation of its alcoholic or ethereal solution, he obtained in the form of needles or prisms melting at 45–46°. The substance was apparently neither analysed nor investigated optically.

A further investigation of these and similar substances has been commenced by us more especially in connection with their optical activity.

#### *Dinitrotartaric Acid.*

We have prepared this acid and have determined its rotatory power in methyl and ethyl alcoholic solutions respectively (for details, see p. 164).

The rotations for a 9 per cent. solution are as follows:

|                             | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-----------------------------|---------------------------|----------------------|
| Methyl alcohol .....        | + 13.70°                  | + 32.88°             |
| Ethyl        „        ..... | + 13.48                   | + 32.35              |

The introduction of the two NO<sub>2</sub> groups thus raises the dextro-

rotation very considerably, for it has been shown that tartaric acid itself is almost destitute of rotatory power in ethyl and methyl alcoholic solutions (Biot, *Mém. de l'Acad.*, 1838, 15, 240), and also in acetone (Landolt, *Ber.*, 1880, 13, 2332).

Comparing the influence of the two  $\text{NO}_2$  groups with that of two acetyl and two benzoyl radicles respectively, it is seen that the two  $\text{NO}_2$  groups have an opposite effect to the two latter pairs of groups, thus:

| Substance.              | Solvent.       | $c$ .  | $l$ . | $[\alpha]_D$ . | $[M]_D$ . |
|-------------------------|----------------|--------|-------|----------------|-----------|
| Diacetyltartaric acid * | Water          | 17.947 | 22°   | -23.04°        | -53.9°    |
| " "                     | "              | 11.486 | "     | -22.16         | -51.9     |
| " "                     | "              | 7.351  | "     | -21.33         | -49.9     |
| " "                     | "              | 4.705  | "     | -20.07         | -47.0     |
| " "                     | Methyl alcohol | 4.681  | 15    | -23.74         | -55.6     |
| " "                     | Ethyl alcohol  | 7.367  | 22    | -23.63         | -55.3     |
| " "                     | "              | 3.274  | "     | -21.52         | -50.4     |
| Dibenzoyltartaric acid† | Methyl alcohol | 4.625  | 19    | -122.14        | -437.3    |
| " "                     | Ethyl alcohol  | 8.506  | 17    | -116.47        | -417.0    |
| " "                     | "              | 4.755  | 15    | -117.68        | -421.3    |

\* Pictet, *Jahrb.*, 1882, 556.

† *Ibid.*

#### *Dimethyl Dinitrotartrate.*

This was also found to be dextrorotatory in methyl and ethyl alcohols, as well as in benzene solution. Thus for an approximately 9 per cent. solution, the following rotations were obtained:

|                                 | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|---------------------------------|---------------------------|----------------------|
| Methyl alcohol .....            | +19.54°                   | +52.37°              |
| Ethyl " .....                   | +14.73                    | +39.48               |
| Benzene, 7.5 per cent. solution | +19.52                    | +52.31               |

The presence of the two  $\text{NO}_2$  groups tends thus again to increase the dextrorotation, for liquid dimethyl tartrate gives, according to Pictet,  $[\alpha]_D^{20^\circ} + 2.14^\circ$  and  $[M]_D^{20^\circ} + 3.81^\circ$ , whilst in benzene solution (Freundler, *Thèses*, Paris, 1894)  $c = 5.5958$ ,  $[\alpha]_D^{24^\circ} - 5.1^\circ$ .

Again, comparing the influence of the two  $\text{NO}_2$  groups with that exerted by pairs of other acid groups on the rotation of dimethyl tartrate, we have:



| Substance.                                     | Solvent.      | c.     | t.   | $[\alpha]_D$ . | $[M]_D$ . |
|--|---------------|--------|------|----------------|-----------|
| Dimethyl diacetyltartrate .....                | Ethyl alcohol | 2.4813 | 25°  | -15.1°         | -39.6°    |
| „ dipropionyltartrate.....                     | Liquid        | —      | 15   | -10.7          | -31.0     |
| „ „ .....                                      | Ethyl alcohol | 5.3025 | 15   | -12.4          | -36.0     |
| „ dibutyryltartrate.....                       | Liquid        | —      | 13   | -15.1          | -48.0     |
| „ „ .....                                      | Ethyl alcohol | 5.8317 | 19   | -12.6          | -40.1     |
| „ diisobutyryltartrate ...                     | „             | 5.9942 | 17   | -13.4          | -42.6     |
| „ divaleryl tartrate .....                     | Liquid        | —      | 15   | -16.1          | -55.7     |
| „ „ .....                                      | Ethyl alcohol | 5.5769 | 19   | -12.9          | -44.6     |
| „ diisovaleryl tartrate.....                   | Liquid        | —      | 14.5 | -13.9          | -48.1     |
| „ „ .....                                      | Ethyl alcohol | 5.4791 | 19   | -9.4           | -32.5     |
| „ dicaproyltartrate.....                       | Liquid        | —      | 13   | -15.9          | -59.5     |
| „ „ .....                                      | Ethyl alcohol | 5.579  | 18   | -12.4          | -46.4     |
| Dimethyl dibenzoyltartrate.....                | Liquid        | —      | 100  | -72.6          | -280.1    |
| „ „ .....                                      | Ethyl alcohol | 0.245  | —    | -96.6          | -372.9    |
| „ di-o-toluyltartrate .....                    | Liquid        | —      | 19   | -78.4          | -324.7    |
| „ „ .....                                      | „             | —      | 100  | -68.0          | -281.6    |
| „ di-m-toluyltartrate .....                    | „             | —      | 100  | -79.0          | -327.1    |
| „ di-p-toluyltartrate .....                    | „             | —      | 100  | -102.8         | -425.7    |
| „ „ .....                                      | Ethyl alcohol | 0.866  | 16   | -108.7         | -450.0    |
| Dimethyl dimonochloroacetyl-<br>tartrate ..... | Liquid        | —      | 20   | -0.64          | -2.12     |
| Dimethyl didichloroacetyltartrate.             | „             | —      | 20   | +11.9          | +47.6     |
| „ diphenacetyltartrate ...                     | „             | —      | 18   | +14.5          | +60.0     |
| „ „ .....                                      | Ethyl alcohol | 0.8873 | 16   | +19.7          | +81.6     |

Thus, whilst the introduction of the two  $\text{NO}_2$  groups into dimethyl tartrate increases the dextrorotation of the latter, it will be seen from the above table that all the other acid groups, excepting phenacetyl and dichloroacetyl, lead to a lævorotation, the latter being most marked in the case of the aromatic acyl radicles. The introduction of two monochloroacetyl groups into dimethyl tartrate exerts only a very slight lævorotatory influence, and thus bridges over the difference in effect between the acetyl radicle and most other acyl groups on the one hand, and the dichloroacetyl, phenacetyl, and  $\text{NO}_2$  groups on the other.

#### *Diethyl Dinitrotartrate.*

This was found to be even more dextrorotatory than the dimethyl compound. Thus the fused solid gave  $[\alpha]_D^{30^\circ} +25.73^\circ$  and  $[M]_D^{30^\circ} +76.16^\circ$ , whilst an approximately 9 per cent. solution gave the following rotations:

|                      | $[\alpha]_D^{30^\circ}$ . | $[M]_D^{30^\circ}$ . |
|----------------------|---------------------------|----------------------|
| Methyl alcohol ..... | +27.18°                   | +80.45°              |
| Ethyl „ .....        | +24.27                    | +71.84               |
| Benzene.....         | +23.76                    | +70.33               |

The effect produced by introducing the two  $\text{NO}_2$  groups into diethyl tartrate is thus also dextrorotatory, for liquid diethyl tartrate, according to Pictet, gives  $[\alpha]_D^{20} + 7.66^\circ$  and  $[M]_D^{20} + 15.8^\circ$ .

(For a very full account of the rotation of diethyl tartrate in various solvents, see Patterson, Trans., 1901, 79, 198.)

The influence of the two  $\text{NO}_2$  groups on the rotation of diethyl tartrate may be compared with that exerted by other acid radicles by means of the following table:

| Substance.                                    | Solvent.      | c.       | t.   | $[\alpha]_D$ . | $[M]_D$ . |
|---|---------------|----------|------|----------------|-----------|
| Diethyl diacetyltartrate ... ..               | Liquid        | —        | 20°  | —              | +9.9°     |
| " " .....                                     | Ethyl alcohol | 7.038    | 25   | +0.4°          | +1.16     |
| " dipropionyltartrate .....                   | Liquid        | —        | 16   | +0.4           | +1.27     |
| " " .....                                     | Ethyl alcohol | 5.5841   | 17   | +1.2           | +3.82     |
| " dibutyryltartrate .....                     | Liquid        | —        | 16   | -0.8           | -2.77     |
| " diisobutyryltartrate .....                  | Ethyl alcohol | 5.50     | 19   | +0.3           | +1.04     |
| " " .....                                     | Liquid        | —        | 17.5 | -1.5           | -5.19     |
| " " .....                                     | Ethyl alcohol | 5.7572   | 19   | +1.4           | +4.84     |
| " divaleryltartrate .....                     | Liquid        | —        | 15   | -2.0           | -7.48     |
| " " .....                                     | Ethyl alcohol | 5.5839   | 18   | -0.7           | -2.62     |
| " diisovaleryltartrate .....                  | Liquid        | —        | 16   | -1.4           | -5.24     |
| " " .....                                     | Ethyl alcohol | 5.4255   | 19   | +0.5           | +1.87     |
| " dicaproyltartrate .....                     | Liquid        | —        | 16   | -3.1           | -12.46    |
| " " .....                                     | Ethyl alcohol | 4.560    | 16   | -1.1           | -4.42     |
| Diethyl dibenzoyltartrate .....               | Liquid        | —        | 18   | -59.36         | -245.7    |
| " " .....                                     | Ethyl alcohol | 9.200    | —    | -68.43         | -283.3    |
| " di-o-toluyltartrate .....                   | Liquid        | —        | 30   | -60.33         | -266.7    |
| " " .....                                     | "             | —        | 100  | -54.73         | -241.9    |
| " di-m-toluyltartrate .....                   | "             | —        | 20.5 | -69.31         | -306.4    |
| " " .....                                     | "             | —        | 100  | -63.74         | -281.7    |
| " di-p-toluyltartrate .....                   | "             | —        | 100  | -89.98         | -397.7    |
| " " .....                                     | Ethyl alcohol | 0.8694   | 16   | -89.1          | -393.8    |
| " dipyromucyltartrate .....                   | Liquid        | —        | 20   | -81.56         | -321.4    |
| " " .....                                     | "             | —        | 99.5 | -67.65         | -266.5    |
| " " .....                                     | Ethyl alcohol | 4.936(p) | 20   | -86.82         | -342.1    |
| Diethyl dimonochloroacetyl-<br>tartrate ..... | Liquid        | —        | 20   | +7.67          | +27.5     |
| Diethyl didichloroacetyltartrate...           | "             | —        | 20   | +16.3          | +69.8     |
| " diphenacetyltartrate .....                  | "             | —        | 20   | +17.9          | +79.2     |
| " " .....                                     | "             | —        | 100  | +9.0           | +39.9     |

Thus, just as in the substitution of dimethyl tartrate, the dichloroacetyl, phenacetyl, and  $\text{NO}_2$  groups form exceptions in exerting a dextrorotatory influence, the other acyl groups exerting a lævorotatory effect, which is again most pronounced in the case of the aromatic radicles. It is noteworthy also that the monochloroacetyl groups, which, in substituting dimethyl tartrate, exert a slight lævorotatory influence, exercise a distinctly dextrorotatory effect in substituting diethyl tartrate.

Considerable difficulty was experienced in obtaining reliable rotatory values for the dinitro-compounds in the alcoholic solutions, owing to the comparatively rapid spontaneous decomposition which these bodies undergo, more especially in ethyl alcohol solution. The mononitro-compounds, on the other hand, are much more stable, and no change in the rotation of their alcoholic solutions was observed, even after such a considerable interval of time as forty-eight hours.

#### *Dimethyl Mononitrotartrate.*

This was also found to be dextrorotatory, in fact, considerably more so than dimethyl dinitrotartrate, excepting in benzene solution. Thus a 9 per cent. solution gave the following rotations :

|                        | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------|---------------------------|----------------------|
| Methyl alcohol .....   | + 28.31°                  | + 63.13°             |
| Ethyl     ,,     ..... | + 27.36                   | + 61.01              |
| * Benzene.....         | + 16.53                   | + 36.86              |

The only other known monoacyl derivative of dimethyl tartrate is dimethyl monotrichloroacetyl tartrate, which in the liquid state has  $[\alpha]_D^{20^\circ} + 8.4^\circ$  and  $[M]_D^{20^\circ} + 27.17^\circ$ .

The trichloroacetyl group thus resembles the nitro-group in exercising a dextrorotatory influence, although a much smaller one, on being introduced into dimethyl tartrate.

#### *Diethyl Mononitrotartrate.*

This again proved to be more dextrorotatory than the diethyl dinitrotartrate. An 8.4 per cent. solution in benzene gave  $[\alpha]_D^{20^\circ} + 31.31^\circ$  and  $[M]_D^{20^\circ} + 78.59^\circ$ ; a methyl alcohol solution (8.9 per cent.) gave  $[\alpha]_D^{20^\circ} + 35.55^\circ$  and  $[M]_D^{20^\circ} + 89.23^\circ$ ; and an 8.5 per cent. ethyl alcohol solution gave  $[\alpha]_D^{20^\circ} + 34.44^\circ$  and  $[M]_D^{20^\circ} + 86.44^\circ$ .

This rotation can be compared with those of a number of monoacyl derivatives of diethyl tartrate which are now known; the rotations are recorded in the following table, along with those of the corresponding diacyl derivatives, the figures being those given by McCrae and Patterson (Trans., 1900, 77, 1108):

\* This determination was made in a 1.765 per cent. solution, this being the strongest that could be used.



|                                     | $[M]_D^{20^\circ}$ |                                      | $[M]_D^{20^\circ}$ |
|-------------------------------------|--------------------|--------------------------------------|--------------------|
| Diethyl tartrate .....              | +15·86°            | Diethyl diacetyltartrate .....       | +9·9°              |
| „ monoacetyltartrate.....           | +23·1              | „ dimonochloroacetyl-                |                    |
| „ monomonochloroacetyl-             |                    | tartrate ... ..                      | +27·5              |
| tartrate .....                      | +32·3              | Diethyl didichloroacetyltartr-       |                    |
| Diethyl monotrichloroacetyl-        |                    | ate .....                            | +69·8              |
| tartrate .....                      | +54·7              | Diethyl diphenacetyltartrate...      | +79·2              |
| Diethyl monophenacetyltartrate      | +98·5              | „ dibenzoyltartrate .....            | -247·1             |
| „ monobenzoyltartrate ...           | +61·4              | „ di- <i>o</i> -toluyltartrate ..... | -266·5             |
| „ mono- <i>o</i> -toluyltartrate... | +38·2              | „ di- <i>m</i> -toluyltartrate.....  | -306·3             |
| „ mono- <i>m</i> -toluyltartrate..  | +44·0              | „ di- <i>p</i> -toluyltartrate ..... | -484·4             |
| „ mono- <i>p</i> -toluyltartrate .. | +63·5              |                                      |                    |

From the above table, it is apparent, as pointed out by McCrae and Patterson, that the diacyl derivative is invariably less, sometimes enormously less, dextrorotatory than the corresponding monoacyl derivative, and the same relationship is now found to hold good for the dinitro- and mononitro-derivatives of both dimethyl and diethyl tartrates respectively. It should be pointed out that this is the first case in which both the di- and the mono-acyl derivatives of dimethyl tartrate are known, all attempts to prepare monoacyl derivatives of the dimethyl ester having hitherto proved abortive, the diacyl compound being formed instead (P. Frankland and McCrae, *Trans.*, 1898, **73**, 310), whilst in the case of the trichloroacetyl derivative only the mono-compound is obtained either from the dimethyl or the diethyl ester (P. Frankland and Patterson, *Trans.*, 1898, **73**, 185).

## EXPERIMENTAL.

### *Dinitrotartaric Acid.*

The method of preparation adopted was that described by Kekulé (*Annalen*, 1883, **221**, 245—246). The ethereal extract was evaporated under diminished pressure, a crop of slightly yellow crystals being obtained. On recrystallisation from ether (purified by sodium) a colourless product was obtained, but as it had no definite melting point it was twice crystallised from pure ether before analysis:

- I. 0·1813 gave 18·4 c.c. moist nitrogen at 22° and 749·6 mm.  $N = 11·32$ .  
 II. 0·2010 „ 20·4 c.c. „ „ 21° and 751·0 mm.  $N = 11·41$ .  
 $C_4H_4O_{10}N_2$  requires  $N = 11·61$  per cent.

The acid, which does not give off nitrous fumes, is very soluble in methyl and ethyl alcohols and ether, but not soluble to any extent either in benzene or chloroform. For polarimetric determinations, see p. 164.

*Diethyl Dinitrotartrate.*

On attempting to prepare this according to Henry's instructions (*Ber.*, 1870, 3, 532), a thick, yellow oil was obtained which soon exhibited signs of decomposition. Repeated solution in ether and alcohol and evaporation of the solvent did not lead to the solidification of the oil. We determined, therefore, to use a lower temperature in the process of nitration.

Thirty grams of diethyl tartrate, possessing the correct rotatory power, were cooled to  $0^{\circ}$  by means of ice-water, and then gradually added to an ice cold mixture of 150 grams of pure sulphuric acid and 150 grams of fuming nitric acid, which was kept well shaken, the temperature being maintained below  $4^{\circ}$  or  $5^{\circ}$  during the process. The emulsion resulting from this was gradually poured into a large volume of iced water, ice being also added from time to time so as to prevent the temperature from rising above  $5^{\circ}$ . Under these conditions, an oil separated and solidified to a visibly crystalline mass, which was repeatedly washed with ice cold water, pieces of ice being introduced in order to disintegrate it. The mass was collected and dried as completely as possible by suction; it was then pressed between filter-paper and recrystallised. On attempting to crystallise from absolute alcohol, signs of decomposition were apparent, so that ether, which had been purified by sodium, was used for the purpose. Latterly, dry chloroform was employed for this crystallisation. The crystals were colourless, flat, needle-shaped prisms, soluble in methyl and ethyl alcohols, benzene, chloroform, and carbon disulphide, but apparently insoluble in water. The substance quietly burns away when heated on platinum foil, and melts, but does not explode, when struck on an anvil. The melting point was  $27^{\circ}$ , and this was not altered by further crystallisation. This melting point is, however, very different from that given by Henry, namely,  $45-46^{\circ}$ , the latter being about the temperature at which we found the mononitrate to melt (see page 163):

0.0928 gave 7.7 c.c. moist nitrogen at  $13.5^{\circ}$  and 742.2 mm.  $N = 9.55$ .

$C_8H_{12}O_{10}N_2$  requires  $N = 9.46$  per cent.

The substance reduces Fehling's solution in a few minutes in the cold and immediately on heating.

The yield under the above conditions was 60—70 per cent. An inferior yield was obtained on using nitric acid of sp. gr. 1.4 instead of the fuming acid. The yield was also diminished by allowing the mixture of diethyl tartrate and acids to stand, and after 14 hours there was, on subsequent mixture with water, no separation of solid at all.

The fused substance was examined at  $30^{\circ}$  in a polarimeter tube 43.67 mm. long;  $d30^{\circ}/4^{\circ} = 1.3147$ ,  $[\alpha]_D + 14.71$ .

$$[\alpha]_D^{30^{\circ}} + 25.62^{\circ}$$

$$[M]_D^{30^{\circ}} + 75.84^{\circ}$$

With a specimen recrystallised from ether the polarimetric result was

$$[\alpha]_D^{30^{\circ}} + 25.73^{\circ}$$

$$[M]_D^{30^{\circ}} + 76.16^{\circ}$$

and this remained practically unaltered after a further crystallisation from the same solvent.

For additional polarimetric determinations in solution, see p. 166.

### *Dimethyl Dinitrotartrate.*

The preparation was carried out in the manner described above for the ethyl compound. The dimethyltartrate, when shaken with the mixed nitric and sulphuric acids, yielded a clear solution, which on pouring into ice water deposited a light, pulverulent, white solid, which, after recrystallisation from pure ether, melted at  $75^{\circ}$ . The crystals were similar in appearance to those of the ethyl compound, only smaller; they were soluble in ethyl and methyl alcohols, ether, chloroform, carbon disulphide, and benzene. The ester was precipitated from its benzene solution by adding ligroin, and again found to have the same melting point. • Latterly, carbon disulphide was always employed for crystallisation. It is not soluble to any appreciable extent in water, and resembles the ethyl compound in not exhibiting any explosive properties:

0.4150 gave 36.5 c.c. moist nitrogen at  $13^{\circ}$  and 761.7 mm.  $N = 10.41$ .

$C_6H_8O_{10}N_2$  requires  $N = 10.45$  per cent.

Under the above experimental conditions, the yield was about 37 per cent., and as it was but slightly lessened when water at the ordinary temperature was used instead of ice water, the latter was generally dispensed with in the preparation of this nitro-compound.

It was found impossible to measure the rotation in the fused state, as the ester underwent decomposition even at  $75.5^{\circ}$ , becoming yellow and evolving gas in the polarimeter tube. Its rotatory power in solution is given on p. 165.

### *Dimethyl Mononitrotartrate.*

Thinking that the large volume of water used in the preparation of the dimethyl dinitrotartrate might contain some of the latter in solution and thus account for the small yield, it was saturated with common salt and repeatedly extracted with ether. The extract, which was yellow in colour, when dried with anhydrous sodium sulphate, and allowed to evaporate *in vacuo*, deposited yellow crystals in consider-



able quantity. After one crystallisation from ether, the substance, which proved to be dimethyl mononitrotartrate, became colourless and had a constant melting point, without decomposition, of  $94.5-95.5^{\circ}$ .\*

0.1676 gave 9.4 c.c. moist nitrogen at  $21^{\circ}$  and 749.0 mm.  $N = 6.29$ .

$C_6H_8O_8N$  requires  $N = 6.28$  per cent.

The substance, which crystallises in white crusts, is soluble in water, ethyl and methyl alcohols, ether, chloroform, and benzene. It decomposes slowly at  $100^{\circ}$ , but a fairly satisfactory polarimetric observation at  $98^{\circ}$  was possible ( $l = 49.91$  mm. ;  $\alpha_D + 18.08^{\circ}$ ).

#### *Diethyl Mononitrotartrate.*

The discovery of the dimethyl mononitrotartrate naturally led us to look for the corresponding diethyl compound in the similar aqueous liquid obtained in the preparation of the diethyl dinitrotartrate. It was similarly isolated as a yellow oil which deposited crystals on standing in an exsiccator for several days, whilst in most of the subsequent preparations the crystals were obtained at once. These crystals, after two crystallisations from pure ether, melted at  $46-47^{\circ}$ . A further purification was effected by shaking them with a considerable volume of water, the undissolved portion being discarded as probably consisting for the most part of the dinitro-compound; the solution was then agitated with ether, the extract dried with sodium sulphate, and evaporated. The crystals thus obtained melted almost sharply at  $47^{\circ}$ , and proved on analysis to be diethyl mononitrotartrate:

0.2004 gave 10.1 c.c. moist nitrogen at  $16.5^{\circ}$  and 736 mm.  $N = 5.67$ .

$C_8H_{13}O_8N$  requires  $N = 5.58$  per cent.

More recently, this substance was extracted from the aqueous liquid by means of chloroform, and on evaporating off the latter under reduced pressure an oil remained which, after about four weeks, deposited transparent, prismatic plates melting at  $27^{\circ}$ . On placing these crystals on a porous plate, they were, in the course of a single night, partially transformed, by spontaneous disintegration, into a white, apparently amorphous mass; the change, thus begun, was greatly accelerated by rubbing with a spatula, the transformation being com-

\* In a later preparation (B), this nitro-ester was obtained by crystallisation from benzene in large, colourless prisms melting at  $97^{\circ}$ . It was this specimen that was employed for the polarimetric determinations in benzene solution (see p. 166). We have lately found it most advantageous to extract the original aqueous solution with chloroform instead of ether, and then the crystals, which separate after evaporating to a small bulk, are recrystallised from benzene.

plete in a few minutes. This amorphous material melted at  $48.5^{\circ}$  and, on being recrystallised from benzene or chloroform, colourless, prismatic crystals were obtained which also melted at  $48.5^{\circ}$ . In fact, the unstable crystals of low melting point were only obtained from the oil in the first instance. The purity of this preparation was also attested by analysis :

0.1947 gave 9.3 c.c. moist nitrogen at  $12^{\circ}$  and 750 mm.  $N = 5.59$ .

$C_8H_{13}O_8N$  requires  $N = 5.58$  per cent.

The yield of this diethyl mononitrotartrate is about 20 per cent. The crystals are soluble in water, ethyl and methyl alcohols, and very soluble in chloroform. The substance is most advantageously recrystallised from carbon disulphide, in which it is sparingly soluble in the cold. From the coincidence in the melting point, it would appear probable that it was this mononitrate, and not the dinitrate, which was obtained by Henry, who gave no analysis of his product.

For polarimetric measurements of the benzene solution, see p. 167.

In the cold the mononitrate reduces Fehling's solution in the course of one hour, and immediately on warming :

*Rotation of Dinitrotartaric Acid.*

| <i>p.</i>                       | <i>d</i> $20^{\circ}/4^{\circ}$ . | <i>t</i> °.  | <i>l</i><br>in mm. | $\alpha_D$ .    | $[\alpha]_D$ .   | $[M]_D$ .        |
|---------------------------------|-----------------------------------|--------------|--------------------|-----------------|------------------|------------------|
| <i>Methyl alcohol solution.</i> |                                   |              |                    |                 |                  |                  |
| 0.9901                          | 0.7972                            | $20^{\circ}$ | 299.84             | $+0.39^{\circ}$ | $+16.48^{\circ}$ | $+39.55^{\circ}$ |
| 4.781                           | 0.8160                            | ,,           | ,,                 | $+1.61$         | $+13.76$         | $+33.02$         |
| 9.0909                          | 0.8359                            | ,,           | ,,                 | $+3.12$         | $+13.70$         | $+32.88$         |
| <i>Ethyl alcohol solution.</i>  |                                   |              |                    |                 |                  |                  |
| 0.9901                          | 0.7981                            | $20^{\circ}$ | 299.84             | $+0.33^{\circ}$ | $+13.93^{\circ}$ | $+33.43^{\circ}$ |
| 4.781                           | 0.8148                            | ,,           | ,,                 | $+1.55$         | $+13.27$         | $+31.85$         |
| 9.0909                          | 0.8356                            | ,,           | ,,                 | $+3.07$         | $+13.48$         | $+32.35$         |

*Rotation of Dimethyl Dinitrotartrate.*

| <i>p.</i>                       | <i>d</i> 20°/4°. | <i>t</i> °. | <i>l.</i><br>mm. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |  |
|---------------------------------|------------------|-------------|------------------|--------------|----------------|-----------|--|
| <i>Methyl alcohol solution.</i> |                  |             |                  |              |                |           |  |
| 0.9901                          | 0.7969           | 20°         | 299.84           | +0.47°       | +19.87°        | +53.25°   | Preparation A.   |
| 4.7810                          | 0.8115           | „           | „                | +2.28        | +19.60         | +52.53    | „  |
| 9.0909                          | 0.8293           | „           | „                | +4.42        | +19.54         | +52.37    | „  |
| 8.3760                          | 0.8273           | „           | 299.3            | +4.21        | +20.28         | +54.35    | Preparation B.   |
| <i>Ethyl alcohol solution.</i>  |                  |             |                  |              |                |           |  |
| 0.9901                          | 0.7963           | 20°         | 299.84           | +0.29°       | +12.27°        | +32.88°   | Preparation A.   |
| 4.7810                          | 0.8123           | „           | „                | +1.60        | +13.74         | +36.82    | „  |
| 9.0909                          | 0.8292           | „           | „                | +3.33        | +14.73         | +39.48    | „  |
| 3.6980                          | 0.8081           | „           | 299.3            | +1.31        | +14.64         | +39.24    | { Preparation B.<br>(Rotation determined<br>within half<br>an hour of<br>making solution.) |
| 8.6030                          | 0.8271           | „           | „                | +2.85        | +13.36         | +35.80    |  |
| <i>Benzene solution.</i>        |                  |             |                  |              |                |           |  |
| 1.0940                          | 0.8828           | 20°         | 389.9            | +0.89°       | +23.63°        | +63.33°   | Preparation C.   |
| 4.1190                          | 0.8928           | „           | 299.3            | +2.32        | +21.08         | +56.49    | „  |
| 5.0980                          | 0.8964           | „           | 389.9            | +3.65        | +20.49         | +54.91    | „  |
| 7.5300                          | 0.9047           | „           | 299.3            | +3.98        | +19.52         | +52.31    | Preparation B.   |
| 8.0230                          | 0.9064           | „           | „                | +4.23        | +19.42         | +52.05    | Preparation C.   |



*Rotation of Diethyl Dinitrotartrate.*

| <i>p.</i>                       | <i>d</i> 20°/4°. | <i>t</i> °. | <i>l.</i><br>mm. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |   |
|---------------------------------|------------------|-------------|------------------|--------------|----------------|-----------|---|
| <i>Methyl alcohol solution.</i> |                  |             |                  |              |                |           |   |
| 1·3170                          | 0·8019           | 20°         | 389·9            | +1·08°       | +26·18°        | +77·49°   | Preparation C.<br>(Specially purified from possible contamination with mononitro-compound by washing with water after crystallisation from chloroform.) |
| 4·6720                          | 0·8119           | „           | „                | +4·01        | +27·13         | +80·30    |   |
| 8·8720                          | 0·8280           | „           | 299·3            | +5·98        | +27·18         | +80·45    |   |
| <i>Ethyl alcohol solution.</i>  |                  |             |                  |              |                |           |   |
| 1·1320                          | 0·7960           | 20°         | 389·9            | +0·90°       | +25·62°        | +75·84°   |   |
| 5·1550                          | 0·8078           | „           | „                | +4·03        | +24·84         | +73·53    |   |
| 8·6430                          | 0·8215           | „           | 299·3            | +5·16        | +24·27         | +71·84    |   |
| <i>Benzene solution.</i>        |                  |             |                  |              |                |           |   |
| 1·0890                          | 0·8814           | 20°         | 389·9            | +0·97°       | +25·94°        | +76·78°   | „   |
| 4·6640                          | 0·8922           | „           | „                | +4·07        | +25·09         | +74·27    | „   |
| 9·3930                          | 0·9062           | „           | „                | +7·88        | +23·76         | +70·33    | „   |

*Rotation of Dimethyl Mononitrotartrate.*

| <i>p.</i>                       | <i>d</i> 20°/4°. | <i>t</i> °. | <i>l.</i><br>in mm. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |                |
|---------------------------------|------------------|-------------|---------------------|--------------|----------------|-----------|----------------|
| <i>Methyl alcohol solution.</i> |                  |             |                     |              |                |           |                |
| 0·9901                          | 0·7961           | 20°         | 299·84              | +0·68°       | +28·77°        | +64·16°   | Preparation A. |
| 4·781                           | 0·8100           | „           | „                   | +3·23        | +27·82         | +62·04    | „              |
| 9·0909                          | 0·8268           | „           | „                   | +6·38        | +28·31         | +63·13    | „              |
| 4·924                           | 0·8139           | „           | 299·3               | +3·29        | +27·43         | +61·17    | Preparation B. |
| <i>Ethyl alcohol solution.</i>  |                  |             |                     |              |                |           |                |
| 0·9901                          | 0·7973           | 20°         | 299·84              | +0·58°       | +24·50°        | +54·64°   | Preparation A. |
| 4·781                           | 0·8101           | „           | „                   | +3·11        | +26·78         | +59·72    |                |
| 9·0909                          | 0·8271           | „           | „                   | +6·17        | +27·36         | +61·01    |                |

*Rotation of Dimethyl Mononitrotartrate (continued).*

| <i>p.</i>                | <i>d</i> 20°/4°. | <i>t</i> °. | <i>l.</i><br>in mm. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |  |
|--------------------------|------------------|-------------|---------------------|--------------|----------------|-----------|--|
| <i>Benzene solution.</i> |                  |             |                     |              |                |           |  |
| 0.9655                   | 0.8855           | 20°         | 389.9               | +0.57°       | +17.07°        | +38.07°   | Preparation B.<br>(Owing to the slight solubility in benzene, stronger solutions could not be employed.) |
| 1.504                    | 0.8869           | "           | "                   | +0.87        | +16.73         | +37.31    |  |
| 1.765                    | 0.8880           | "           | "                   | +1.01        | +16.53         | +36.86    |  |

*Rotation of Diethyl Mononitrotartrate.*

| <i>p.</i>                       | <i>d</i> 20°/4°. | <i>t</i> °. | <i>l.</i><br>mm. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |  |
|---------------------------------|------------------|-------------|------------------|--------------|----------------|-----------|--|
| <i>Methyl alcohol solution.</i> |                  |             |                  |              |                |           |  |
| 1.0590                          | 0.8092           | 20°         | 389.9            | +1.22°       | +36.40°        | +91.36°   | Preparation B.   |
| 4.6610                          | 0.8208           | "           | 299.3            | +4.05        | +35.41         | +88.88    | "  |
| 8.9080                          | 0.8352           | "           | "                | +7.92        | +35.55         | +89.23    | "  |
| <i>Ethyl alcohol solution.</i>  |                  |             |                  |              |                |           |  |
| 1.1210                          | 0.7949           | 20°         | 389.9            | +1.21°       | +34.78°        | +87.30°   | Preparation C.   |
| 4.4440                          | 0.8055           | "           | 299.3            | +3.67        | +34.22         | +85.89    | "  |
| 8.5250                          | 0.8191           | "           | "                | +7.20        | +34.44         | +86.44    | "  |
| <i>Benzene solution.</i>        |                  |             |                  |              |                |           |  |
| 4.8082                          | 0.8909           | 20°         | 299.3            | +4.20°       | +32.77°        | +82.25°   | Preparation B.   |
| 5.0810                          | 0.8909           | "           | "                | +4.42        | +32.60         | +81.83    | " C.   |
| 6.1071                          | 0.8950           | "           | "                | +5.23        | +31.96         | +80.22    | " A.<br>(Recrystallised from benzene many months after preparation.) |
| 8.4564                          | 0.9014           | "           | "                | +7.14        | +31.31         | +78.59    | Preparation B.   |

#### XIV.—*The Nitration of Diethyl Monobenzoyl- and Mono-p-toluyll-tartrates.*

By PERCY FARADAY FRANKLAND, HENRY LEONARD HEATHCOTE, B.Sc.,  
and CLARENCE JAMES GREEN, B.Sc.

##### *Diethyl Mononitrobenzoyltartrate and Diethyl Mononitro-p-toluyll-tartrate.*

THESE compounds were obtained from diethyl monobenzoyltartrate and diethyl mono-*p*-toluylltartrate respectively, by treating them with a mixture of nitric and sulphuric acids in the cold on the chance of thus obtaining mononitrates. In both cases, however, the NO<sub>2</sub> group entered the benzene ring, and by hydrolysis it was shown that the *m*-nitrobenzoyl group was present in the one, and the nitro-*p*-toluyll group (CH<sub>3</sub>:NO<sub>2</sub>:CO = 1:2:4) in the other.

The rotatory power of these compounds was greatly affected by the nature of the solvent in which the rotation was determined (for details, see p. 173).

The rotation of the diethyl mono-*m*-nitrobenzoyltartrate is of interest in connection with that of the mono-*m*-toluylltartrate, as these two compounds enable a comparison to be instituted between the respective rotatory effects of the CH<sub>3</sub> and the NO<sub>2</sub> groups occupying the same position in the benzene ring. The comparison is, however, attended with great difficulty, owing to the variable rotation of the diethyl mono-*m*-nitrobenzoyltartrate in different solvents; the diethyl mono-*m*-toluylltartrate was only polarimetrically examined in the fused state and in glacial acetic acid solution (see P. Frankland and McCrae, Trans., 1898, 73, 322). The molecular rotation of fused diethyl mono-*m*-toluylltartrate at 20° is +44·0°, whilst in glacial acetic acid only about +25°, so that, on the whole, the rotatory effect of the nitro-group would appear to be greater than that of the methyl group occupying the same position in the molecule. A much more detailed investigation, however, will have to be made in order to complete the comparison between these two groups.

The same comparison may also be instituted by means of the three diethyl ditoluylltartrates and the three dinitrobenzoyltartrates respectively, and also between the three similar pairs of dimethyl esters. The diethyl and dimethyl nitrobenzoyltartrates have been prepared and polarimetrically examined by one of us in conjunction with Dr. Harger, and the results will form the subject of a future communication. It will be sufficient here to remark that these compounds furnish overwhelming evidence that the NO<sub>2</sub> group exercises a higher rotatory effect than the CH<sub>3</sub> group occupying the same position in the benzene ring.



Again, the relative rotatory effects of the  $\text{NO}_2$  and methyl groups may be ascertained from another series of comparisons, namely, dinitrotartaric acid and dimethoxysuccinic acid, dimethyl dinitrotartrate and dimethyl dimethoxysuccinate, diethyl dinitrotartrate and diethyl dimethoxysuccinate. The above derivatives of dimethoxysuccinic acid have recently been prepared and most fully described by Purdie, Irvine, and Barbour (*Trans.*, 1901, **79**, 973), and on comparing their figures with those found by us for the dinitrotartrates, it is obvious that in all cases dimethoxysuccinic acid and its esters have much higher molecular rotations, of the same sign, than the corresponding derivatives of dinitrotartaric acid. Thus, in this series, the methyl group exercises a much more powerful, although similar, rotatory effect than does the nitro-group occupying the same position in the molecule.

We append Purdie and Irvine's figures for the rotation of the corresponding dimethoxy-compounds, in order to compare these with our rotatory values given in the preceding communication for dinitrotartaric acid and its derivatives :

*Dimethoxysuccinic Acid.*

|                                | $[\alpha]_D^{20^\circ}$ | $[M]_D^{20^\circ}$ |
|--------------------------------|-------------------------|--------------------|
| Water solution, $c = 17.5839$  | + 72.28°                | + 128.7°           |
| 8.9104                         | + 74.74                 | + 133.0            |
| 4.4570                         | + 75.39                 | + 134.2            |
| 1.7812                         | + 76.63                 | + 136.4            |
| Acetone solution, $c = 8.9091$ | + 89.29                 | + 158.9            |
| 3.5595                         | + 91.30                 | + 162.5            |
| 1.7797                         | + 95.80                 | + 170.5            |

*Dimethyl Dimethoxysuccinate.*

*Diethyl Dimethoxysuccinate.*

|          |               | $[\alpha]_D^{60^\circ}$ | $[M]_D^{60^\circ}$ |               |        | $[\alpha]_D^{20^\circ}$ | $[M]_D^{20^\circ}$ |
|----------|---------------|-------------------------|--------------------|---------------|--------|-------------------------|--------------------|
|          |               | + 82.52°                | + 170.0°           |               |        | 89.7                    | 209.9°             |
| Solvent. |               | $[\alpha]_D^{20^\circ}$ | $[M]_D^{20^\circ}$ |               |        | $[\alpha]_D^{20^\circ}$ | $[M]_D^{20^\circ}$ |
| Water    | $c = 19.9988$ | + 78.71°                | + 162.1°           | $c = 5.3752$  |        | 89.11°                  | 208.5°             |
|          | 10.0315       | 78.45                   | 161.6              |               |        |                         |                    |
|          | 5.0319        | 78.50                   | 161.7              |               |        |                         |                    |
| Benzene  | $c = 20.0036$ | 101.63                  | 209.4              | $p = 19.3137$ | 102.65 | 240.2                   |                    |
|          | 10.0128       | 104.66                  | 215.6              | 10.1117       | 104.14 | 243.7                   |                    |
|          | 5.0060        | 105.47                  | 217.3              | 5.3130        | 104.93 | 245.1                   |                    |
| Methyl   |               |                         |                    |               |        |                         |                    |
| alcohol  | $p = 23.0151$ | 78.90                   | 162.5              | $p = 19.0407$ | 87.27  | 204.2                   |                    |
|          | 12.0806       | 76.32                   | 157.2              | 9.7865        | 87.41  | 204.5                   |                    |
|          | 6.2598        | 81.04                   | 166.9              | 6.0569        | 87.66  | 205.1                   |                    |

Thus whilst the  $\text{NO}_2$  group attached to the benzene ring has hitherto exhibited a higher rotatory effect than  $\text{CH}_3$  similarly attached, the comparison of nitrotartaric acid and its esters with the dimethoxysuccinates shows that the  $-\text{O}\cdot\text{CH}_3$  group has a higher rotatory effect than the  $-\text{O}\cdot\text{NO}_2$  group in these compounds.

On the other hand, it will be shown by one of us, later, that  $\text{NO}_2$  attached to the benzene ring has a greater rotatory effect than  $-\text{O}\cdot\text{CH}_3$  similarly combined.

The difference in the relation between the rotatory effects of the  $\text{NO}_2$  and  $\text{CH}_3$  groups, according as they are directly attached to the benzene ring or united to carbon by means of oxygen, may depend on differences in the structure of the  $\text{NO}_2$  group in the nitro-compounds and nitrates respectively.

The diethyl mono-*m*-nitrobenzoyltartrate and the corresponding di-*m*-nitrobenzoyltartrate enable us again to test the regularity pointed out by McCrae and Patterson with regard to the effect of the single and double substitution of diethyltartrate, and to which reference has already been made on p. 160 in the preceding communication. Thus, it will be seen that the introduction of a single *m*-nitrobenzoyl group produces a greater dextrorotatory change than the addition of two such groups; in fact, diethyl di-*m*-nitrobenzoyltartrate is powerfully lævorotatory. These results are thus in conformity with the above generalisation.

The rotation of diethyl mononitro-*p*-toluyltartrate is again extraordinarily dependent on the solvent, being dextrorotatory in ethyl alcohol, ethyl acetate, and chloroform, whilst it is lævorotatory in benzene and especially so in pyridine solution.

## EXPERIMENTAL.

### *Diethyl Mono-m-nitrobenzoyltartrate.*

In the hope of possibly obtaining a benzoylmononitrotartrate, diethyl monobenzoyltartrate was nitrated, but the reactions of the product show that the nitro-group enters the benzene ring, forming instead  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{O}\cdot\text{CO}\cdot\overset{(1)}{\text{C}}_6\text{H}_4\cdot\overset{(8)}{\text{NO}}_2)\cdot\text{CO}_2\text{Et}$ .

Diethyl monobenzoyltartrate, of melting point  $65\cdot5^\circ$  and rotation  $[\alpha]_D^{26} + 17\cdot68$  (P. Frankland and McCrae, Trans., 1898, 73, 310), was added in small quantities at a time and with constant stirring to a mixture of five times its weight of fuming nitric acid (sp. gr. 1·52), the temperature being kept below  $5^\circ$  by means of an ice jacket. The mixture was then poured slowly into water containing ice, which was kept constantly stirred so that the temperature did not rise above  $8^\circ$ . The thick, oily product which separated soon became solid (amounting

to 85—90 per cent. of the theoretical yield) and was collected and washed with water until the washings showed only a faint acid reaction. The solid was dried on porous plates and then dissolved in benzene; the filtered solution, when treated with low boiling ligroin until a faint milkiness was produced, slowly yielded a solid crystallising in long, flexible, silky needles melting at  $113^{\circ}$ ,\* and soluble in alcohol, benzene, pyridine, chloroform, and ethyl acetate, but almost insoluble in cold carbon disulphide and ligroin :

0.2747 gave 9.8 c.c. moist nitrogen at  $18^{\circ}$  and 750 mm.  $N = 4.06$

0.1352 „ 0.2525  $CO_2$  and 0.0605  $H_2O$ .  $C = 50.94$ ;  $H = 4.97$ .

$C_{15}H_{17}O_9N$  requires  $N = 3.94$ ;  $C = 50.70$ ;  $H = 4.79$  per cent.

The results of the polarimetric determinations made with solutions of this ester are given on p. 173.

The substance did not reduce Fehling's solution even on heating. It was easily hydrolysed with alcoholic potash, slowly even in the cold and very rapidly on warming. After hydrolysis, the alcohol was distilled off and the residual potassium salts dissolved in water. On adding hydrochloric acid, a solid at once separated; this was filtered off and crystallised from hot water, by which means it was obtained in long needles melting at  $141^{\circ}$ . The melting points of *o*-, *m*-, and *p*-nitrobenzoic acids are  $147^{\circ}$ ,  $141^{\circ}$ , and  $238^{\circ}$  respectively. The crystals had thus the melting point of *m*-nitrobenzoic acid, and the analysis of the silver salt gave the following confirmatory result :

0.0998 gave 0.0396 Ag.  $Ag = 39.68$ .

$C_6H_4NO_2 \cdot CO_2Ag$  requires  $Ag = 39.39$  per cent.

The filtrate from the *m*-nitrobenzoic acid was in one case neutralised with ammonia and treated with a solution of calcium chloride. The precipitate formed was calcium tartrate :

0.2465 gave 0.1307  $CaSO_4$ .  $Ca = 15.58$ .

$CaC_4H_4O_6 \cdot 4H_2O$  requires  $Ca = 15.38$  per cent.

The tartaric acid contained in another portion of the filtrate from the *m*-nitrobenzoic acid was converted into potassium hydrogen tartrate :

0.3475 gave 0.1666  $K_2SO_4$ .  $K = 21.50$ .

$KHC_4H_4O_6$  requires  $K = 20.74$  per cent.

In order to ascertain whether racemisation had occurred in the preparation, this potassium hydrogen tartrate was examined polarimetrically in aqueous solution at  $20^{\circ}$  :

\* Miss Hattle subsequently obtained a melting point of  $113.5^{\circ}$  by crystallising from glacial acetic acid.



0.57 gram in 100 grams solution :  $d_{20}^{40} = 0.9973$  ;  $l = 299.84$  mm.,  $\alpha_D + 0.36^\circ$  ;  $[\alpha]_D^{20} + 21.12^\circ$ .

Landolt (*Opt. Drehungsvermögen*, 2nd. edit., p. 492) gives

$$c = 0.615, t = 20^\circ [\alpha]_D^{20} + 22.61^\circ,$$

from which it is evident that the product was practically unracemised potassium hydrogen tartrate. The slight deficiency in the dextro-rotation and the high percentage of potassium were probably due to the salt containing a little potassium chloride.

*Diethyl mononitro-p-toluyltartrate*, obtained by nitrating diethyl mono-*p*-toluyltartrate in the manner described in the preparation of the corresponding benzoyl compound, exactly resembles the latter in appearance and melts at  $104\text{--}105^\circ$ , the yield being 80—90 per cent. of the theoretical :

0.2471 gave 8.3 c.c. moist nitrogen at  $15^\circ$  and 751 mm.  $N = 3.89$ .

0.2565 „ 8.95 c.c. „ „ „  $17^\circ$  „ 747 mm.  $N = 3.79$ .

0.1022 „ 0.1936  $\text{CO}_2$  and 0.0495  $\text{H}_2\text{O}$ .  $C = 51.66$  ;  $H = 5.38$ .

$\text{C}_{16}\text{H}_{19}\text{O}_9\text{N}$  requires  $N = 3.79$  ;  $C = 52.03$  ;  $H = 5.15$  per cent.

The results of the polarimetric determinations made on solutions of the above are given in the table on p. 173.

By hydrolysis with alcoholic potash, tartaric and nitrotoluic acids were obtained, and these were separated from each other owing to the slight solubility of the latter in cold water. The melting point of the nitrotoluic acid was  $186^\circ$  (uncorr.), and corresponds closely with that of the nitro-*p*-toluic acid [ $\text{Me} : \text{NO}_2 : \text{CO}_2\text{H} = 1 : 2 : 4$ ] prepared by Ahrens (*Zeit. f. Chem.*, 1869, 5, 104), which is stated to melt at  $189\text{--}190^\circ$ ;

| Solvent.                                    | Grams of substance in 100 grams of solution.<br><i>p.</i> | Density<br>20°/4°. | <i>l.</i><br>mm. | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|---|---|--------------------|------------------|-------------------------|---------------------------|----------------------|
| <i>Diethyl mono-m-nitrobenzoyltartrate.</i> |   |                    |                  |                         |                           |                      |
| Ethyl alcohol.....                          | 2.3810  | 0.7954             | 299.84           | +0.71°                  | +12.50°                   | +44.38°              |
| „ acetate.....                              | 4.9675  | 0.9113             | „                | +3.60                   | +26.52                    | +94.15               |
| „ „.....                                    | 2.6870  | 0.9048             | „                | +2.17                   | +29.77                    | +105.68              |
| Chloroform.....                             | 4.0420  | 1.4700             | „                | +2.54                   | +14.26                    | +50.62               |
| „ „.....                                    | 2.8560  | 1.4743             | „                | +1.92                   | +15.21                    | +54.00               |
| Benzene.....                                | 2.9994  | —                  | „                | ±0                      | ±0                        | ±0                   |
| Pyridine.....                               | 9.0020  | 0.9986             | „                | +1.26                   | +4.64                     | +16.47               |
| „ „.....                                    | 4.3900  | 0.9865             | „                | +0.71                   | +5.47                     | +20.42               |
| <i>Diethyl mononitro-p-toluyltartrate.</i>  |   |                    |                  |                         |                           |                      |
| Ethyl alcohol.....                          | 2.6261  | 0.7957             | 299.84           | +0.44°                  | +7.02°                    | +25.90°              |
| „ „.....                                    | 1.7370  | 0.7926             | „                | +0.29                   | +7.02                     | +25.90               |
| „ acetate.....                              | 8.9295  | 0.9240             | „                | +4.91                   | +19.85                    | +73.25               |
| „ „.....                                    | 3.6266  | 0.9081             | „                | +1.85                   | +18.73                    | +69.11               |
| Chloroform.....                             | 7.6555  | 1.4594             | „                | +5.61                   | +16.74                    | +61.77               |
| „ „.....                                    | 4.7648  | 1.4670             | „                | +3.50                   | +16.70                    | +61.62               |
| „ „.....                                    | 2.9640  | 1.4727             | „                | +2.18                   | +16.66                    | +61.47               |
| Benzene.....                                | 3.8838  | 0.8855             | „                | -1.12                   | -10.86                    | -40.07               |
| Pyridine.....                               | 7.0502  | 0.9915             | „                | -4.30                   | -20.51                    | -75.68               |
| „ „.....                                    | 4.2367  | 0.9858             | „                | -2.58                   | -20.60                    | -76.01               |
| „ „.....                                    | 3.1842  | 0.9836             | „                | -1.92                   | -20.45                    | -75.46               |

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## XV.—*The Hydrates and the Solubility of Barium Acetate.*

By JAMES WALKER and WILLIAM A. FYFFE.

BARIUM acetate is well known to exist in three modifications, two of which are hydrated and one anhydrous. Thus it is stated in Gmelin's *Handbook* that when left to evaporate spontaneously in summer, the concentrated aqueous solution deposits crystals containing one molecule of water, whilst a less concentrated solution cooled to 0° yields

crystals containing three molecules of water. At 100°, the anhydrous salt is obtained.

The older data concerning the solubility of barium acetate are somewhat discrepant. It is stated in Kolbe's *Lehrbuch*, on the authority of Liebig, that the substance is more soluble in cold water than in hot. Bucholz (quoted in Storer's *Dictionary of Solubilities*) states, on the other hand, that the crystals (monohydrate ?) dissolve in 2.25 parts of water at the ordinary temperature and in 1.1 parts at the boiling point. Storer also quotes from Berzelius's *Lehrbuch* that the saturated cold solution contains 36 per cent., and the saturated boiling solution 50 per cent.

Tilden and Shenstone determined the solubility of barium acetate at temperatures ranging from 20° to 180° (*Phil. Trans.*, 1884, 175, 23). The curve by means of which they express their results shows a solubility of 48 parts of anhydrous salt in 100 parts of water at 20°, rising rapidly to 79 parts in 100 at 60°, thereafter to continue constant up to 100°. Since, however, Tilden and Shenstone were more immediately concerned with the solubility of the salt above 100°, they only performed three determinations below that temperature, so that the form which they give to their curve in the region below 100° cannot be regarded as conclusive.

Krasnicki (*Monatsh.*, 1887, 8, 601) determined the solubility of barium acetate monohydrate at temperatures between 0° and 80°, and found that his results could be expressed by the formula

$$S = 58.47 + 0.65067(t - 0.8) - 0.005431(t - 0.8)^2,$$

in which  $t$  is the temperature in centigrade degrees and  $S$  the solubility in parts of anhydrous salt dissolved by 100 parts of water. It appeared to us rather remarkable that a substance which was known to exist in two hydrated forms at low temperatures should give a single continuous solubility curve throughout such an extensive range.

From the behaviour of the hydrates detailed in Gmelin's *Handbook* one might expect to deal, between 0° and 100°, with three distinct solubility curves, for the trihydrate, monohydrate, and anhydrous salt respectively, which should cut in two transition points, and the chief object of this investigation was to ascertain if this were the case, and to determine as exactly as possible the transition temperatures for the conversion of trihydrate into monohydrate, and of monohydrate into anhydrous salt.

The barium acetate which we employed in the investigation was always recrystallised by ourselves. When the hot saturated solution was cooled to the laboratory temperature, the trihydrate separated out in needle-shaped crystals. This substance could not be kept in



the dry state, as it speedily effloresced and was partially converted into the monohydrate. The monohydrate which we employed was generally prepared from the trihydrate, this, after two days in an exhausted desiccator, lost two-thirds of its water and was completely converted into monohydrate. Under ordinary laboratory conditions, the monohydrate could be kept indefinitely without undergoing alteration. The anhydrous salt was prepared by heating either of the hydrates in a steam oven for several hours; usually two days were allowed in order to secure complete dehydration.

For the purpose of obtaining an approximate idea of the position of the inversion temperatures, a van't Hoff dilatometer was charged with the trihydrate and toluene. When placed in a thermostat at  $20^{\circ}$ , the reading of the toluene in the capillary remained constant for four hours, thus indicating no transformation at this temperature. At  $35^{\circ}$ , the toluene rose rapidly during the first hour and slowly during the next two hours, thereafter remaining constant for 20 hours. This behaviour indicated that between  $20^{\circ}$  and  $35^{\circ}$  the trihydrate undergoes transformation into a less hydrated form, the transformation being accompanied by an increase of volume. On heating now at  $40^{\circ}$ , no change of volume was observed during 3.5 hours, thus indicating no further transformation. At  $45^{\circ}$ , however, a slow diminution in volume was perceptible, lasting more than 20 hours. This second transformation, thus indicated between  $35^{\circ}$  and  $45^{\circ}$ , is accompanied by a diminution instead of an increase of volume. At  $55^{\circ}$ , no further volume change was observed.

In order to ascertain definitely the nature of the change at these inversion points, the solid, after it had remained in contact with the solution for several hours at different temperatures, was separated and analysed. In each case, the original solid, when brought into contact with the aqueous solution, was transformed into the trihydrate. The analysis was performed by converting the substance into barium sulphate as in the solubility estimations described below:

| Temperature. | Percentage of barium. |                    |
|--------------|-----------------------|--------------------|
|              | Found.                | Calculated.        |
| $0^{\circ}$  | 43.5                  | Trihydrate... 44.3 |
| 16           | 43.7                  |                    |
| 27.4         | 50.0                  | Monohydrate 50.2   |
| 36.5         | 50.1                  |                    |
| 49           | 53.6                  | Anhydrous... 53.7  |

These numbers show beyond doubt that, below the first transition point, the trihydrate is in equilibrium with the solution, whilst the anhydrous salt is in this condition above the second transition point,

the range for the stable existence of the monohydrate in contact with solution being limited by these two temperatures.

To establish the lower transition point more accurately, a fresh dilatometer was charged with trihydrate. From the previous dilatometric experiments and the above analyses we knew that the transition temperature probably lay between  $20^{\circ}$  and  $27^{\circ}$ . First, we found that there was a very pronounced increase of volume at  $27^{\circ}$ , so that this temperature was certainly above the transition point. At  $22^{\circ}$ , there was an equally pronounced diminution in volume, so that this temperature was as certainly below the transition point. At  $24^{\circ}$ , there was a slow but decided contraction; at  $25.5^{\circ}$ , a slow but decided expansion. The transition temperature therefore lay between these limits. Approaching the true inversion point from both sides, we ultimately found that at  $24.5^{\circ}$  there was a very slow diminution of volume, and at  $24.8^{\circ}$  a very slow increase in volume. At  $24.7^{\circ}$  neither expansion nor contraction could be observed. We may therefore conclude that  $24.7^{\circ}$  is the inversion temperature of the system trihydrate-monohydrate, the error in the determination probably not exceeding  $0.1^{\circ}$ .

Much greater difficulty was experienced in fixing accurately the inversion temperature of the system monohydrated-anhydrous salt. This was chiefly due to the comparative sluggishness of the transformation. Previous results had shown that the transition point lay somewhere in the range  $35-45^{\circ}$ , but a dilatometer charged with a mixture of monohydrate and anhydrous salt showed practically no change in volume at any temperature between  $39^{\circ}$  and  $42^{\circ}$ . We then endeavoured to increase the rate of the transformation by substituting a saturated solution of barium acetate for the toluene which we had previously used in the dilatometer. The bulb of a large dilatometer was filled with anhydrous salt in a fine state of division, heated at  $50^{\circ}$ , exhausted, and filled up with a solution of barium acetate saturated at the same temperature. The dilatometer was then placed in a thermostat at  $39.3^{\circ}$ . No very decided change was noted for some hours, but after a day it was observed that several crystals of monohydrate had begun to form. In the course of a week, these had become more than an inch in length, so that the dilatometer had to be broken in order that they might be examined. They proved to be crystals of the monohydrate, which rendered it certain that the temperature of the transition point was above  $39.3^{\circ}$ . At  $40^{\circ}$ , a similar growth of monohydrated crystals at the expense of the anhydrous salt was observed, and, although in this case the growth was much slower, there could be no doubt that the transition temperature was below  $40^{\circ}$ . At  $42^{\circ}$ , no change of anhydrous salt into monohydrate could be observed. On the contrary, a large crystal of the monohydrate, when

heated at this temperature in a test-tube containing xylene, in the course of a few days lost its transparency and showed distinct planes of cleavage. This behaviour indicated incipient transformation into anhydrous salt, and at a somewhat higher temperature the large crystal broke up into numerous small crystals about half a millimetre long, water being at the same time eliminated. The transformation at  $42^{\circ}$  was also confirmed by means of a dilatometer charged with monohydrate, anhydrous salt, and saturated solution, and this mixture showed a slight diminution in volume at  $42^{\circ}$ , that is, the volume change which accompanies the transformation of the monohydrate into anhydrous salt and water. The limits within which the second inversion point must lie are therefore  $40-42^{\circ}$ . We can consequently take  $41^{\circ}$  as the inversion temperature of the system monohydrated-anhydrous salt, with a liability to error probably not exceeding  $1^{\circ}$ . As will be seen later, the solubility data confirm this result.

### *Solubility Experiments.*

The apparatus which we employed for determining the solubility of barium acetate was in all essentials identical with that described by Lumsden (Trans., 1902, 81, 352). At the higher temperatures, however, at which the solution was in contact with finely divided anhydrous salt, a different mode of filtration had to be adopted. During the process of saturation at these temperatures, the stirrer alone passed through the stopper of the bottle containing the solution. A second rubber stopper was provided with a filtering-tube and a short glass tube, which at one end was flush with the lower surface of the stopper, and at the other end was attached to the rubber tube of a hand-blower. The filtering tube was a capillary glass tube blown out at one extremity to a conical shape, a disc of filter paper supported between two discs of muslin being tied over the conical end. About half an hour before it was intended to filter off the solution, the stopper, fitted with the stirrer, was replaced by the stopper furnished with the filtering apparatus. The liquid was forced through the filter by means of the pressure produced by the blower; the first few drops were neglected, and then succeeding portions were delivered directly into the weighed platinum crucibles in which the composition of the solution was determined.

The crucible and its contents were weighed and the solution carefully evaporated to dryness. The evaporation during our first experiments was conducted on the water-bath, but it was found later that the concentration could be conducted much more rapidly and equally satisfactorily as follows. Two discs of asbestos millboard, 3 mm. in thickness, were placed on the bottom of a nickel crucible



about two inches in diameter, and on these the platinum crucible was laid, and then heated very gently by means of a small flame applied to the external nickel crucible. The evaporation proceeded rapidly and with little spirting, although, as a precautionary measure, the lid of the crucible was kept in position during the operation. There was no difficulty in weighing the residue of barium acetate as such; but to secure uniformity in the results the acetate was always converted into sulphate by the addition of concentrated sulphuric acid, the excess of which was driven off in the same manner, a larger flame being of course employed. The crucible containing the dry sulphate was finally heated directly by means of a Teclu burner.

As examples of the agreement obtained in the conversion of the acetate into sulphate, we may take the following. Two solutions, which on evaporation yielded residues of 1.0961 and 1.2522 grams of acetate, gave quantities of barium sulphate corresponding with 1.0969 and 1.2523 grams of the acetate respectively. The evaporation of the solution, conversion into sulphate, and ignition, did not by this method occupy more than an hour.

It was soon apparent after we had begun the solubility estimations that a time of contact, which would have ensured saturation in the case of most substances, was quite insufficient, in the case of barium acetate, to bring about equilibrium between the solid and solution. At low temperatures, the equilibrium between the solution and the trihydrate is established with moderate rapidity, but in the range of temperature including the transition points, and some way on either side, a considerable amount of difficulty was experienced in obtaining saturated solutions.

For example, at 16° the monohydrate after 1.5 hours gave a solubility of 69.0 parts of anhydrous salt in 100 parts of water. After 24 hours, the solubility obtained was 69.3, and after 48 hours, 69.2. The solution was thus practically saturated after one and a half hours' contact with constant stirring. On the other hand, at 41.8° the anhydrous salt after three hours' stirring gave a solubility of 76.7, which rose after 24 hours to 78.0. In every doubtful case we repeated our determinations of the solubility with constantly increasing times of contact until we obtained sufficiently concordant results. The following method gave good results for the anhydrous salt, with which we experienced most difficulty. A stock solution was prepared containing about 60 parts of anhydrous salt dissolved in 100 parts of water. This solution was heated at a temperature somewhat above that at which the determination was to be made, and then mixed with finely powdered anhydrous salt also heated at the same temperature. The solid and solution were vigorously stirred for about four hours, after which a fresh quantity of finely powdered

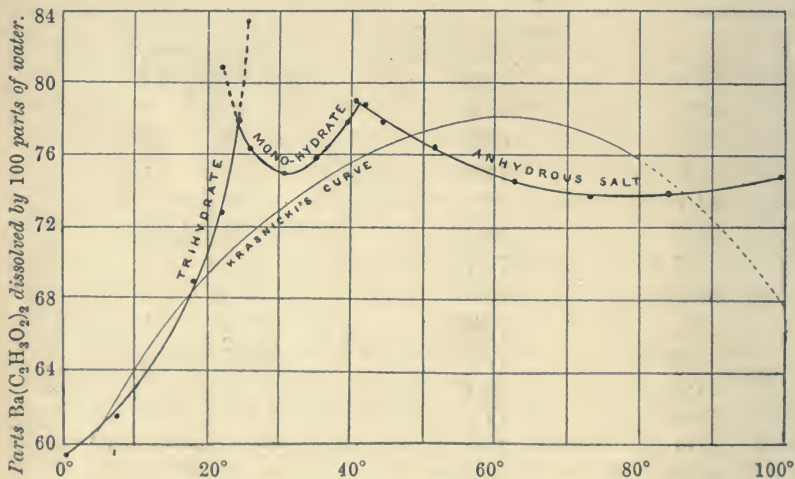
solid was introduced and the stirring continued for another hour. This seemed in every case to bring about saturation. In the majority of cases, parallel experiments were conducted with three bottles of solution in the thermostat in order to assure ourselves that equilibrium had been attained. In one of the bottles, the solid used was the trihydrate, in another the monohydrate, and in the third, the anhydrous salt. For instance, at  $39.6^{\circ}$ , solutions saturated with the monohydrate as original solid gave a mean value for the solubility of 77.6; solutions which were saturated from the trihydrate gave 77.9, and solutions saturated from the anhydrous salt gave 78.2. Here the general mean value of 77.9 certainly represents the true equilibrium concentration with close approximation.

The following table gives our results for the solubility at different temperatures, each value being the mean of several concordant experiments. We are indebted to Mr. F. G. Young for the determinations at the four highest temperatures:

| Temperature.  | Parts $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$<br>in 100 parts of water. | Solid in equilibrium<br>with solution.                             |
|---------------|---|--|
| $0.3^{\circ}$ | 58.8  | $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$ |
| 7.9           | 61.6  | "  |
| 17.5          | 69.2  | "  |
| 21.6          | 72.8  | "  |
| 24.1          | 78.1  | "  |
| 26.2          | 76.4  | $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2, \text{H}_2\text{O}$  |
| 30.6          | 75.1  | "  |
| 35.0          | 75.8  | "  |
| 39.6          | 77.9  | "  |
| 40.5          | 79.0  | $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$                      |
| 41.5          | 78.7  | "  |
| 44.5          | 77.9  | "  |
| 51.8          | 76.5  | "  |
| 63.0          | 74.6  | "  |
| 73.0          | 73.5  | "  |
| 84.0          | 74.0  | "  |
| 99.2          | 74.8  | "  |

When these results are exhibited in curve form (p. 180), it is seen at once that we are dealing with three distinct curves, which intersect at points agreeing with the transition points determined by the dilatometer. Thus the curves for the two hydrates evidently cut each other at a temperature between  $24^{\circ}$  and  $25^{\circ}$ , corresponding with the transition point,  $24.7^{\circ}$ , previously found. Again, the curves for the monohydrate and anhydrous salt intersect at about  $41^{\circ}$ , in accordance with the estimate already given.

We made several attempts to obtain points on the curves in the metastable region beyond the transition points, but only met with success in the case of the lower transition temperature. At  $26.1^{\circ}$ , that is, about  $1.4^{\circ}$  above the first transition point, the transformation of trihydrate into monohydrate is comparatively slow, so that if the pure trihydrate is taken as the original solid, it is possible to obtain a solution considerably more concentrated than that corresponding with the number 76.3, which is the solubility of the stable monohydrate at this temperature. Thus the trihydrate after contact for three and five hours gave the solubilities 81.8 and 83.4 respectively, but after 22 hours' contact the solubility had sunk to 79.4. If we take the maximum number, 83.4, to represent the solubility of the metastable trihydrate, we find that in reality it falls on the prolongation of the trihydrate curve, as shown by the dotted line in the figure.



We were at first unable to secure a point on the monohydrate curve below the transition temperature, but at last succeeded by employing the following device. A porcelain mortar containing some finely powdered anhydrous salt was heated in a thermostat at  $22^{\circ}$ , and into this was introduced about 15 c.c. of a clear saturated solution of barium acetate at the same temperature. When intimately mixed with this solution by means of a pestle, the anhydrous salt was seen to dissolve freely, and after a few minutes the liquid suddenly began to deposit fine crystals of the monohydrate. It was then rapidly filtered and the concentration of the resulting solution ascertained. It was noticed that, before the analysis was made, the filtered solution deposited



a considerable quantity of the crystals of the trihydrate, thus showing that it had been supersaturated with respect to the trihydrate. The number obtained for the solubility was 81.0, which, it will be observed, lies accurately on the prolongation of the monohydrate curve below the transition point.

*Krasnicki's Results.*

It has already been mentioned that Krasnicki obtained results for the solubility of barium acetate which he was able to express with great accuracy by means of a single formula, that is, by a single curve. In order to show to what extent his results differ from our own, we have plotted his curve alongside those which give expression to our experimental data. Krasnicki makes no mention of the trihydrate, but states that barium acetate crystallises with one molecule of water, which it loses at 150°. His solubility experiments were apparently all conducted with the monohydrate as solid. For the attainment of equilibrium he allowed only from one to one and a half hours' shaking. In view of our own experience, this is altogether insufficient for the establishment of equilibrium at temperatures above 20°. Below that temperature, the results agree moderately well, above that temperature there is no further agreement except at about 47°, where the two curves intersect. It is remarkable that Krasnicki should have obtained concordant results from experiments made by heating and also by cooling solutions to the temperature at which saturation was desired, and further that his experimental results should diverge from those calculated from his formula by less than 0.1 per cent. in every case.

In order to test in a simple way between Krasnicki's results and our own, we saturated a solution at 100°, filtered, and allowed the clear solution to cool slowly. According to Krasnicki's curve, no solid would be deposited until the solution had cooled to at least 40°, and when once the solid had appeared, its quantity would constantly augment as the cooling proceeded. According to our curves, a small quantity of solid should appear after the solution had cooled only slightly, and this should then disappear at a temperature somewhere below 60°, no further solid appearing until the temperature had fallen to nearly 20°. What we actually observed was that crystals appeared in the solution when it had cooled to 84°. These crystals remained undissolved until the temperature had fallen to 49°, at which point the solution again became perfectly clear, to remain so until the room temperature was attained. No trihydrate had separated even after 24 hours, but the introduction of a minute fragment of this substance at once induced crystallisation. This experiment alone shows that Krasnicki's results for the higher temperatures are invalid.

*Summary.*

Dilatometric and solubility experiments show that the transition temperature from  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  to  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  is  $24.7^\circ$ , and that the transition temperature from  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  to  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  is  $41^\circ$ .

The solubility is not expressed, as Krasnicki found, by a single curve concave to the temperature axis, but by three independent curves, convex to the temperature axis, and intersecting at the transition points. The curve for the monohydrate shows a minimum at about  $30^\circ$ , and the curve for the anhydrous salt a minimum at about  $75^\circ$ .

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## XVI.—*The State of Carbon Dioxide in Aqueous Solution.*

By JAMES WALKER.

WHEN carbon dioxide is dissolved in water, a portion is converted into carbonic acid,  $\text{H}_2\text{CO}_3$ ; and from the conductivity data of Knox (*Ann. Phys. Chim.*, 1895, 54, 44) and Walker and Cormack (*Trans.*, 1900, 77, 8) it appears that the acid accurately obeys Ostwald's dilution law.

Reasoning on the assumption that the amount of carbonic acid, dissociated and undissociated, was proportional to the amount of unchanged carbon dioxide in the solution, I showed that Ostwald's dilution law would not hold good for the range of dilution investigated, unless the proportion of the carbonic acid to the carbon dioxide were greater than one-fourth, and assumed that the same result would follow, at least for moderate dilutions, on the more probable hypothesis that the amount of undissociated carbonic acid only was proportional to the unchanged carbon dioxide.

Professor Abegg, of Breslau, who has worked at the similar problem of the state of ammonia in aqueous solution, kindly drew my attention to the fact that, on the second assumption, the deduction is not valid. The true dilution law for such a case may be deduced simply from the law of mass action without neglect of terms as follows.

Consider 1 gram-mol. of carbon dioxide dissolved in water, so as to form  $v$  litres of solution. Let  $a$  = number of gram-mols. of

unchanged  $\text{CO}_2$ ;  $b$  = number of gram-mols. of undissociated  $\text{H}_2\text{CO}_3$ ;  $m$  = number of gram-mols. of dissociated  $\text{H}_2\text{CO}_3$ ; then

$$a + b + m = 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the equilibrium between  $\text{CO}_2$  and undissociated  $\text{H}_2\text{CO}_3$ , we have, according to Guldberg and Waage's law,  $\frac{a}{v} = r \frac{b}{v}$ , where  $r$  is a constant, or  $b = \frac{a}{r}$ .

Equation (1) therefore becomes

$$a + \frac{a}{r} + m = 1, \text{ or } \frac{a}{r} (1 + r) = 1 - m,$$

and

$$b = \frac{a}{r} = \frac{1 - m}{1 + r} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the equilibrium between the undissociated and dissociated  $\text{H}_2\text{CO}_3$ , we have, according to the same law,

$$\left(\frac{m}{v}\right)^2 = k' \frac{b}{v},$$

where  $k'$  is a constant. Substituting the value of  $b$  in (2), we obtain

$$\left(\frac{m}{v}\right)^2 = k' \frac{1 - m}{(1 + r)v},$$

or

$$\frac{m^2}{(1 - m)v} = \frac{1}{1 + r} k' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since both  $r$  and  $k'$  are constant, equation (3) expresses Ostwald's dilution law,

$$\frac{m^2}{(1 - m)v} = k,$$

in which  $k$  is the apparent dissociation constant found from measurements of the conductivity (compare Walker and Cormack, *loc. cit.*, p. 10). The constant  $k'$  is the real dissociation constant of carbonic acid, and is related to  $k$  by the equation

$$k' = (1 + r)k,$$

$1 + r$  being the constant ratio of the total non-ionised substance to the non-ionised but hydrated acid. For dilutions at which the degree of dissociation is small, this relation is identical with that previously given (Walker and Cormack, *loc. cit.*, p. 13).

It is evident from this that no conclusion can be drawn as to the degree of hydration of carbon dioxide (or any similar substance) in



aqueous solution from the mere fact that Ostwald's dilution law is obeyed, for the law of mass action leads to this relation whatever may be the degree of hydration.

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DUNDEE.

## XVII.—*Qualitative Separation of Arsenic, Antimony, and Tin.*

By JAMES WALKER.

THE following method for the separation of arsenic, antimony, and tin has been tested for more than a year in my laboratory, and has been found to give good results in the hands of moderately careful workers. It differs from the ordinary methods chiefly in this, that the tin is first separated from the arsenic and antimony, instead of being left as a residue, which frequently escapes detection if the tin was originally present in small quantity. As an alternative method, therefore, it may be found of service in many cases.

If the sulphides of arsenic, antimony, and tin are dissolved in caustic soda, and if the solution thus obtained is boiled with sodium peroxide, the sulphides pass ultimately into sodium arsenate, antimonate and stannate. Now stannic acid is a much feeble acid than either arsenic or antimonie acid—so feeble, indeed, that it is incapable of forming in solution, a stable salt with a weak base like ammonia. If, therefore, a solution containing sodium stannate is boiled with excess of ammonium chloride, double decomposition occurs, and the ammonium stannate which is produced decomposes with evolution of ammonia, stannic acid (stannic hydroxide) being at the same time precipitated. The sodium salts of arsenic and antimonie acids are not decomposed by ammonium chloride in this way, so that advantage may be taken of this difference in order to effect a separation of tin from arsenic and antimony. The separation is not quantitative, as a little antimony is usually found in the tin precipitate, but for qualitative purposes it is perfectly satisfactory. No trouble has been experienced from the formation of insoluble sodium metantimonate.

In order that the arsenic group may be in a state suitable for treatment with sodium peroxide, caustic soda (or potash) should be used. The effect the separation of the sulphides of the copper from those of the law of group. In connection with this, the following points have

Consider 1. Firstly, stannous sulphide is often very imperfectly as to form  $v$  10 caustic alkali. This difficulty may be overcome by

adding a few drops of yellow ammonium sulphide to the caustic alkali used in treating the mixed sulphides. The accumulation of sulphur in the filtrate, which occurs when ammonium sulphide alone is employed in the separation, is thereby avoided, and subsequent operations are in consequence simplified. Secondly, mercuric sulphide readily dissolves in caustic soda when sulphides of the arsenic group are present. This solvent action is caused by excess of caustic soda reacting partially with the sodium thio-salts of the arsenic group to form sodium sulphide, in a solution of which mercuric sulphide is freely soluble. When such a solution, however, is boiled with sodium peroxide, the sodium sulphide is oxidised to sodium sulphate, and the mercuric sulphide is reprecipitated. Details of the actual operations are given in the following paragraphs.

*Separation and Oxidation of the Arsenic Group.*—The precipitate of mixed sulphides is diluted with a little water in a porcelain basin, and caustic soda solution is gradually added to the hot liquid until no more precipitate seems to dissolve, any large excess of caustic soda being avoided. Three or four drops of yellow ammonium sulphide solution are then added, and the liquid boiled until it no longer smells of ammonia. The solution is now diluted with warm water, and the copper group precipitate filtered off and washed.

The filtrate contains the arsenic group and, possibly, mercury. After further dilution, it is heated to the boiling point in a porcelain basin, and sodium peroxide gradually added in small quantities to the gently boiling solution until there is a permanent effervescence of oxygen, showing that excess of peroxide is present. If mercury was contained in the alkaline solution, it now appears as a black precipitate of mercuric sulphide, which is filtered off and tested separately. The filtrate then contains only sodium arsenate, antimonate, and stannate.

*Separation of Tin from Antimony and Arsenic.*—The filtrate is transferred to a beaker and gently boiled after the addition of solid ammonium chloride; this salt must be in considerable excess, about three times the bulk of the sodium peroxide employed being generally sufficient. If tin is present, it separates as a white, gelatinous precipitate. A further amount of ammonium chloride is added to see if the precipitate increases in bulk, and boiling is continued for about five minutes in order that the precipitate may coagulate, after which it is collected. Greatly prolonged boiling is inadvisable, as the liquid then filters rather slowly. The precipitate should be washed with warm water containing in solution a little ammonium chloride.

*Confirmation of Tin.*—The precipitate is dissolved on the filter in a few drops of warm concentrated hydrochloric acid, a solution of stannic chloride being thereby produced. A portion of the solution

may then be tested with sulphuretted hydrogen, which gives a yellow precipitate of stannic sulphide. The remainder of the solution should be reduced from the stannic to the stannous state, this operation being best effected by means of iron as recommended by Bloxam. Zinc is so strongly electropositive that it not only reduces the stannic compound to the stannous state, but precipitates metallic tin. Copper, on the other hand, cannot precipitate the metal, being electronegative to tin, but, in consequence, the reduction to the stannous state is slow. Iron is intermediate between these two metals, being close to tin in the electrochemical list, and slightly positive to it. It therefore easily reduces stannic to stannous tin, but does not readily precipitate metallic tin from the acid stannous solution. In effecting the reduction, the stannic solution, strongly acidified with hydrochloric acid, is heated to the boiling point with the iron. At first the solution assumes a yellow colour, owing to the formation of ferric chloride, but this colour disappears in a few moments and the reduction of the stannic compound proceeds. Unless iron filings are known to be pure, it is inadvisable to use them for the reduction. Iron wire acts well, though somewhat slowly. If rapid reduction is required, reduced iron (*ferrum redactum*) may be employed. With reduced iron, the operation does not take more than a minute; with iron wire, the solution should be allowed to stand for five minutes. After the excess of iron has been removed, by filtration if necessary, one portion of the solution is treated with sulphuretted hydrogen, which gives a brown precipitate of stannous sulphide, and the remainder is tested with mercuric chloride. Ammonium molybdate cannot, in this case, be used to detect the stannous compound, as a blue coloration is sometimes produced even when tin is absent.

*Separation of Antimony and Arsenic.*—The filtrate from the tin precipitate contains arsenic and antimony in the form of arsenate and antimonate respectively. These may be separated by Bunsen's method by means of sulphuretted hydrogen as follows. The solution is acidified with hydrochloric acid and warmed until oxygen ceases to be evolved. It is then cooled and treated with a rapid current of sulphuretted hydrogen. Antimony, if present, is at once precipitated as an orange or golden-yellow sulphide, which may be filtered off and confirmed in the ordinary way. To the filtrate, which ought to smell feebly of sulphuretted hydrogen, a few drops of sodium thiosulphate solution are added, and the solution is warmed until a precipitate begins to separate. Sulphuretted hydrogen is then passed through the solution. If the precipitate which separates is white, it consists merely of sulphur; if bright yellow, it contains arsenious sulphide, which may be filtered off and confirmed in the ordinary manner,



Sometimes the yellow precipitate of arsenious sulphide is produced on warming with the sodium thiosulphate, but its quantity is usually increased by subsequent treatment with sulphuretted hydrogen.

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### XVIII.—*A Reagent for the Identification of Urea and Certain other Nitrogen Compounds.*

By HENRY J. HORSTMAN FENTON, F.R.S.

A CONSIDERABLE number of new derivatives of methylfurfural have recently been described in communications to the Society by Miss Gostling and the author (Trans., 1899, 75, 423, 1901, 79, 807, &c.). The starting point for the preparation of these compounds is the bromo-derivative,  $\text{O}:\text{CH}\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CH}_2\text{Br}$ , or the corresponding chloro-derivative; these compounds are easily obtained by the action of the dry halogen acids on ketohexoses or on cellulose.

Amongst the various compounds obtained from these derivatives, a condensation product was described having the formula  $\text{C}_{11}\text{H}_8\text{O}_4$ , the constitution of which is still under investigation, but which would appear, from the evidence so far obtained, to be either methyl-furil,  $\text{C}_4\text{H}_3\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CH}_3$ , the dialdehyde,  $\text{CH}_2(\text{C}_4\text{H}_2\text{O}\cdot\text{CH}:\text{O})_2$ , or the ketonealdehyde,  $\text{O}:\text{CH}\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CO}\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CH}_3$ .

[The second formula is perhaps the least probable owing to the striking difference in properties between this compound and the dialdehyde  $\text{O}:\text{CH}\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{H}_2\text{O}\cdot\text{CH}:\text{O}$  previously described, *loc. cit.*, 1901, 812.]

This compound crystallises in long, transparent, pale yellow needles which melt at  $117^\circ$ ; it dissolves sparingly in hot water and is easily soluble in chloroform or hot benzene, alcohol, and other organic solvents. It gives very beautiful colour reactions with certain nitrogen compounds and the colours produced are so intense that the reactions afford extremely delicate tests for these compounds.

If the reagent be ground together with urea and the mixture treated with phosphorus oxychloride, acetyl chloride, or dry hydrogen chloride, a beautiful Prussian blue colour is developed. In using the reaction as a test for urea the solids are well mixed together, or if the substance to be examined is in solution it is mixed with an alcoholic solution of the reagent and evaporated to dryness on the water-bath.

The phosphorus oxychloride (or other agent mentioned) may conveniently be dissolved in an appropriate solvent, such as light petroleum, glacial acetic acid or benzene.

When applied in this manner, the reaction is so delicate that even 0.1 mm. of urea gives a strongly marked colour and it is easy, with care, to detect 0.01 mm. or less.

Monomethyl urea, monoethyl urea, and monophenyl urea all give exactly similar reactions. Allantoin,  $\text{CO} \begin{array}{l} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CONH}_2 \end{array}$ , behaves similarly, but the colour appears more slowly, and biuret,  $\text{NH}_2 \cdot \text{CONH} \cdot \text{CONH}_2$ , gives only a faint blue colour on long standing.

Urethane,  $\text{NH}_2 \cdot \text{CO} \cdot \text{OEt}$ , develops an intense coloration which is blue by reflected and red by transmitted light. Sodium carbamate behaves similarly. The colour obtained with urethane is also immediately produced even when *aqueous* hydrogen chloride is used as the condensing agent.

No trace of a blue coloration was obtained with any of the following: *sym.* diphenylurea  $\text{NHPh} \cdot \text{CO} \cdot \text{NHPh}$ , *unsym.* dimethylurea,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe}_2$ , monoacetylurea, acetylmethylurea,  $\text{NHAc} \cdot \text{CO} \cdot \text{NHMe}$ , oxaluric acid,  $\text{NH}_2\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , uric acid, alloxan, parabanic acid, cyanuric acid, cyanamide, formamide, acetamide, acetanilide, oxamide, succinamide, benzamide, semicarbazide, and glycine, although many of these substances decidedly react giving various shades of yellow, brown, &c. Thiourea gives a slight greenish colour.

The blue coloration obtained in the above-mentioned cases is found to be due to the formation of colourless bases which give, with acids, salts having an intense blue colour. These bases may be easily separated by treating the blue salts with moist barium carbonate and extracting with alcohol; the colourless solutions so obtained give the blue colour at once on treatment with aqueous acids, but the intensity of the colour depends in a marked way upon the 'strength' and concentration of the acid; it is most intense with hydrochloric, hydrobromic, sulphuric, and trichloroacetic acids, and is only just perceptible with acetic and tartaric acids. Probably the affinity constants of acids might be compared by a study of these effects.

Preliminary analyses of the urea base indicate that it is formed by condensation of one molecule of the 'reagent'  $\text{C}_{11}\text{H}_8\text{O}_4$  with two molecules of urea, and if the other bases are similarly constituted, this fact accounts for the necessity of the  $\text{NH}_2$  group in the reacting nitrogen compound as seen in the above examples, since the 'reagent' contains two carbonyl groups. The power of producing the *blue* colour would appear to depend on the basic or salt-forming capabilities of the group attached to the  $\text{CONH}_2$  radicle. This would explain the non-

formation of the colour with acyl ureas such as acetylurea or oxaluric acid, whilst in the case of allantoin the group in question might perhaps be expected to be more basic. This 'explanation' is really only a suggestion, and in the case of urethane must probably be of a different order.

The above-mentioned bases are very easily oxidised by exposure to the air, and at present only a superficial examination has been made of them, but since they promise to be of considerable interest it is proposed to make a complete study of some of the most typical ones.

In addition to the method above mentioned, the base from urea has been prepared in the following way. The dry 'reagent' is well ground together with a considerable excess (about three times its weight) of dry urea and the mixture heated over a small flame until it just melts. A dark reddish liquid results which solidifies on cooling, and is dissolved in hot aqueous alcohol. Absolute alcohol, when added to the cooled solution, precipitates a reddish-yellow, amorphous substance, which separates in flocks and is then thoroughly washed several times with the precipitant. This substance, which is nearly insoluble in absolute alcohol or water, even on boiling, dissolves fairly easily in hot aqueous alcohol; and is precipitated from this solution, either by water or alcohol. It is practically insoluble in benzene, chloroform, ethyl acetate and most other organic solvents. Owing to the readiness with which it is oxidised and also to its hygroscopic nature when dried, it is difficult to manipulate for analysis. When dried in a desiccator under diminished pressure, the following result was obtained:

0.1643 gave 27.6 c.c. nitrogen at 19° and 739 mm.  $N = 19.19$ .

$[C_{11}H_8O_4 + 2CO(NH_2)_2 - 2H_2O]$  requires  $N = 19.44$  per cent.

When heated somewhat above 100°, it becomes dark red and afterwards quite black at about 200° without melting. Its solutions in acids have an intense blue colour and show well-marked absorption bands in the red end of the spectrum.

If in preparing this base in the above manner, the temperature becomes too high, or if the heating be long continued, a dark orange-red substance is produced which is practically insoluble in any solvent so far examined.

It was previously pointed out (*loc. cit.*, 1899, 75, 432) that this reagent gives a beautiful green colour with aniline acetate. This colour is produced on simply mixing the solutions, without the use of any condensing agent. Further inquiry shows that this behaviour is characteristic of all primary aromatic and alkyl amines, similar intense green colorations being obtained with *o*- and *p*-toluidines,



*m*-xylidine,  $\alpha$ - and  $\beta$ -naphthylamines, *m*-phenylenediamine, and also with methylamine and ethylamine. The last two, however, give a less intense colour, and the effect generally appears only on warming.

Diphenylamine gives no colour when similarly treated, but it does so if a condensing agent such as phosphorus oxychloride be added.

Negative results are obtained with dimethylaniline, pyridine, hydroxylamine, hydrazine, phenylhydrazine, and guanidine.

This green colour is also due to the formation of colourless bases which give green salts, but in this case the weaker acids give the most intense colorations, excess of strong acid completely destroying this effect.

Most of the expense incurred in carrying out the present investigation has been defrayed out of funds kindly provided by the Government Grant Committee of the Royal Society.

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## XIX.—*Note on the Action of Acids on Cellulose.*

By MILDRED GOSTLING, B.Sc.

IN a previous communication (Fenton and Gostling, *Trans.*, 1901, 79, 361), it has been shown that all forms of cellulose, when heated to about 80° with a saturated solution of hydrochloric or hydrobromic acid in chloroform or carbon tetrachloride, yield  $\omega$ -chlorobromomethylfurfural. It was also shown (*Proc.*, 1901, 17, 166) that dextrose, which could be extracted with water after separation of the methylfurfural derivative, was formed at the same time. These results conclusively proved the presence of a ketose as well as an aldose nucleus in cellulose.

In every case, about 40 per cent. of a black residue which retained the fibrous structure of the original cellulose was also left after the action of the acids.

In the hope of throwing further light on the constitution of cellulose, the nature of this residue was investigated, and in order to ascertain whether it had a constant composition it was necessary to prepare the residue free from any of the original cellulose by repeated treatment with hydrochloric acid until no more of the furfural derivative was formed.

Five grams of pure cotton wool were introduced into a strong glass bottle with a well-ground stopper and covered with about 300 c.c. of carbon tetrachloride, which was then saturated with dry hydro-

chloric acid gas at  $0^{\circ}$ . The stopper was firmly fixed by means of an iron clamp and the mixture heated nearly to boiling in a water-bath for 4 hours; on cooling, the carbon tetrachloride solution was drained off, the residue washed well with ether and with hot water, and then dried in a steam oven. This treatment was repeated until the carbon tetrachloride solution contained no methylfurfural. The black residue so obtained was insoluble in all organic solvents and retained the fibrous structure of the original cotton wool.

Analysis gave  $C = 62.31$  and  $62.51$ ;  $H = 4.29$  and  $4.07$  per cent.

After being once more similarly treated, the results were  $C = 62.21$ ;  $H = 3.68$  per cent.

Pure Swedish filter paper was treated in exactly the same way, and, on analysis, the black residue, which retained the structure of the filter paper, gave  $C = 62.42$  and  $62.70$ ;  $H = 3.64$  and  $3.74$  per cent.

The ordinary cellulose solvents (cuprammonium solution, zinc chloride solution, and acetic anhydride) have no action on this black residue. To make sure that it contained none of the original cellulose, some of the residue from filter paper was heated for half an hour with acetic anhydride and a few drops of concentrated sulphuric acid. It was then collected, washed free from sulphuric acid and acetic anhydride, dried at  $100^{\circ}$ , and now contained  $C = 61.72$ ;  $H = 3.72$  per cent.

$C_{12}H_{10}O_5$  requires  $C = 61.54$ ;  $H = 4.26$  per cent.

Some of the black residue was suspended in water and chlorine passed in for some time; the flask was then closed and allowed to stand for some hours; chlorine was again passed in and the process repeated. The substance, which was still fibrous in character after repeated treatment, acquired a bright yellow colour, and by means of alcohol or ether a small quantity of a bright yellow powder could be extracted. After this extraction, the residue was again subjected to the action of chlorine and more of the yellow powder obtained, but the action, being only a surface one, was very slow.

Experiments with other solvents for chlorine, such as chloroform or carbon tetrachloride, were made, but the action seemed to take place even more slowly. The yellow powder was purified by dissolving it in dry ether and precipitating with petroleum, and several specimens were analysed. The percentage of chlorine ( $Cl = 25.73, 26.1, 26.48, 30.45, 34.00$ , and  $34.35$ ) increased as the substance was repeatedly treated with this reagent, the analyses indicating that probably a mixture of chloro-derivatives is thus produced, these substances being difficult to separate on account of their sparing solubility and uncrystallisable character.

The action of bromine was similar, but was even slower.

Nitric acid (sp. gr. 1.2) and alkaline potassium manganate oxidise the residue to oxalic acid.

The original ~~black residue~~ is quite insoluble in alkalis, water, alcohol, ether, and other organic solvents. The composition and general character of this residue is therefore closely allied to the substances known as artificial humus, obtained by Conrad and Guthzeit (*Ber.*, 1885, 18, 439; 1886, 19, 2844), and by Sestini, by the action of dilute acids on sugars. It corresponds most nearly with sacculmin, prepared by Sestini by boiling cane sugar with dilute sulphuric acid, and described as a black, amorphous mass, insoluble in caustic potash solution, &c., and reacting with chlorine to give yellow, amorphous chloro-compounds. Sestini gives to sacculmin the formula  $C_{44}H_{38}O_{15}$  (carbon, 65.5; hydrogen, 4.8 per cent.), which has a slightly higher percentage of carbon and hydrogen than that found in the black residue from cellulose.

I wish to express my thanks to Mr. Fenton to whom I am greatly indebted for his valuable advice.

The expenses incurred in this work have been defrayed by a grant received from the Government Grant Committee of the Royal Society.

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## XX.—*Purpurogallin.* I.

By ARTHUR GEORGE PERKIN, F.R.S.E., and ALEC BOWRING STEVEN, B.Sc. (Lond.).

THE oxidation products of pyrogallol and its derivatives have received considerable attention, for these substances are not only readily prepared, but show an interesting variation in constitution, less frequently observed with other phenolic compounds. Thus when air is conducted through an alkaline solution of gallic acid in the presence of alcohol (Bohn and Graebe, *Ber.*, 1887, 20, 2328), galloflavin is formed, this product being probably a pentahydroxyxanthonecarboxylic acid, whereas ethyl gallate in the presence of alkalis gives ellagic acid, which is a derivative of fluorene. Again, if pyrogallol is treated with barium peroxide (Harries, *Ber.*, 1902, 35, 2955), hexahydroxydiphenylene ketone is produced, and cedrret or tetramethoxydiphenoquinone is readily prepared by the oxidation of pyrogallol dimethyl ether (Hofmann, *Ber.*, 1878, 11, 335). A most interesting derivative of pyrogallol is purpurogallin, which, unlike the yellow



colouring matter. Attempts to explain their isomerism would have little value closely resembling all been further studied.

been recently studied, *pyrogallin with Zinc Dust*.—Four grams of the information as to its constitution, usual methods, gave a small quantity of the reaction by which it is formed. It solid on standing overnight, yet far from complete, but as Harries (*loc. cit.*) crystallised twice from what similar direction, it appeared advisable to send colourless leaflets, Society.

By treating pyrogallol in acid solution with silver borates the potassium permanganate and sulphuric acid, A. Girard (*Ber.*, 1871, 562) obtained a red substance,  $C_{20}H_{16}O_9$ , which he named purpugallin. A. Wichelhaus (*Ber.*, 1872, 5, 848), by oxidising pyrogallol with quinone, obtained the same substance (pyrogallol quinone) and gave it the formula  $C_{18}H_{14}O_9$ , and the constitution  $OH \cdot C_6H_3[O \cdot O \cdot C_6H_3(OH)_2]_2$ . H. Struve (*Annalen*, 1872, 163, 102) made the interesting discovery that purpugallin is formed by allowing a mixture of pyrogallol and gum arabic solutions to stand for some hours, and he further noticed that blood has a similar effect. On repeating these experiments, Clermont and Chautard (*Jahresb.*, 1882, 682) succeeded in obtaining a yield of 67 per cent. of purpugallin by the gum arabic method. These authors also employed platinum black as oxidising agent and observed the production of carbon dioxide during the formation of purpugallin; they describe a tetra-acetyl derivative,  $C_{20}H_{12}O_9(C_2H_3O)_4$ , m. p.  $186^\circ$ , sodium and barium salts,  $C_{20}H_{12}Na_4O_9$ ,  $C_{20}H_{12}Ba_2O_9$ , and a tetrabromo-compound,  $C_{20}H_{12}Br_4O_9$  (m. p.  $202-204^\circ$ ). With sulphuric acid, purpugallin gave the compound  $C_{20}H_{12}O_{10}$ , and by means of hydriodic acid a mixture of substances,  $(C_{10}H_{14})_n$ , was formed. S. Hooker (*Ber.*, 1887, 20, 3259) employed potassium ferricyanide as the oxidising agent, the yield being 13 to 14 per cent., and he also describes the production of purpugallin by the action of potassium nitrite on a solution of gallic acid in the cold. Nietzki and Steinmann (*Ber.*, 1887, 20, 1277) studied the formation of the colouring matter by means of nitrous acid, and demonstrated that the substance they prepared was identical with pyrogallol quinone (*loc. cit.*). As by distillation with zinc dust they obtained naphthalene, it seemed evident that purpugallin contained this nucleus, and they consider that, during the oxidation of the pyrogallol, some of the benzene nuclei are split up, and that condensation of the product ensues to form this naphthalene ring. Acetyl purpugallin was again examined, and the formula  $C_{20}H_{16}O_9$  considered as probably representing the colouring matter itself.

The action of bromine was similar, but was even slower.

Nitric acid (sp. gr. 1.2) and alkaline peroxide residue to oxalic acid.

The original black residue is a ferricyanide was employed alcohol, ether, and other organic solvents, as Hooker states, of about a yield, as Hooker states, of about 25 per cent. of the crude material, but occasionally as much as 6.5 grams were thus isolated.\* The product, purified by crystallisation from acetic acid containing animal charcoal, was found to consist, as examination of the mother liquors showed, of but one substance :

0.1378 gave 0.3014  $\text{CO}_2$  and 0.0474  $\text{H}_2\text{O}$ .  $\text{C} = 59.66$  ;  $\text{H} = 3.82$ .

$\text{C}_{11}\text{H}_8\text{O}_5$  requires  $\text{C} = 60.00$  ;  $\text{H} = 3.63$  per cent.

$\text{C}_{20}\text{H}_{16}\text{O}_9$  „  $\text{C} = 60.00$  ;  $\text{H} = 4.00$  „

Nietzki and Steinmann found  $\text{C} = 60.04$  ;  $\text{H} = 3.85$  per cent.

Purpurogallin forms orange-red needles closely resembling alizarin in appearance, and is soluble in caustic alkaline solutions with an orange-red coloration, which, owing to oxidation, rapidly become deep blue and finally of a brownish-yellow tint. Clermont and Chautard state that the alkaline solutions of purpurogallin are blue, but this is not the case ; and it will be remembered that other pyrogallol derivatives such as myricetin behave similarly in that the yellow alkaline liquid which first results subsequently develops a blue coloration in contact with air. Purpurogallin melts at  $274\text{--}275^\circ$  with decomposition. It dissolves in sulphuric acid with an orange-red coloration, and if heated at  $140^\circ$ , sulphurous acid is slowly evolved, with formation of Clermont and Chautard's compound  $\text{C}_{20}\text{H}_{12}\text{O}_{10}$  (?), which we are at present examining.

Purpurogallin was unattacked by alcoholic hydrochloric acid at  $150^\circ$  for 3 hours. It possesses well-marked dyeing properties, somewhat resembling those of alizarin, but which have not previously attracted much notice. On mordanted wool, the following shades were obtained :

| Chromium.                | Aluminium.    | Tin.      | Iron.       |
|--------------------------|---------------|-----------|-------------|
| Reddish-chocolate-brown. | Brownish-red. | Brick-red | Deep-black. |

\* Preliminary experiments on the electrolysis of aqueous solutions of pyrogallol containing potassium acetate or acetic acid, kindly carried out for us by Dr. F. M. Perkin, furnished a small quantity of orange-brown substance. As this is possibly purpurogallin, the subject will be further investigated.

Attempts to explain their isomerism would have little value. Could the yield have been further studied.

*Tetra-acetylpurpurogallin* with Zinc Dust.—Four grams of the usual methods, gave a small quantity of boiling acetic anhydride for several hours. The product formed yellow crystals on standing overnight. The product formed yellow crystals, crystallised twice from alcohol. The product formed yellow crystals, crystallised twice from identical with that described by Clermont and Nietzki and Steinmann. Acetyl determinations gave colourless leaflets, with naphthalene, with result:

0.8215 gave 0.4660 purpurogallin Found 56.72.

1.5830 „ 0.9020 „ „ 56.98.

$C_{11}H_4O_5(C_2H_3O)_4$  requires  $C_{11}H_8O_5 = 56.70$  per cent.

$C_{20}H_{12}O_9(C_2H_3O)_4$  „  $C_{20}H_{12}O_9 = 70.42$  „

It is evident therefore that the latter formula cannot be a correct representation for acetylpurpurogallin, and calculation shows that no acetyl derivative of a compound  $C_{20}H_{16}O_9$  could give figures harmonising with this result. Molecular weight determinations of this compound were therefore carried out by the cryoscopic method, employing naphthalene as a solvent:

0.4871, dissolved in 14.75 naphthalene, gave  $\Delta t$  0.568°.  $M = 407$ .

$C_{19}H_{16}O_9$  requires  $M = 388$ .

These results therefore indicate that purpurogallin, is most probably represented by the formula  $C_{11}H_8O_5$ .

*Tribenzoylpurpurogallin* was prepared by Deninger's method. One gram of purpurogallin, dissolved in 15 grams of pyridine, was treated with 12 grams of benzoyl chloride and allowed to stand for 12 hours. The mixture was washed with water, the residue poured into alcohol, and the precipitated benzoyl compound collected and purified by crystallisation from a mixture of cumene and alcohol:

0.1285 gave 0.3392  $CO_2$  and 0.0447  $H_2O$ .  $C = 71.99$ ;  $H = 3.86$ .

$C_{11}H_5O_5(C_7H_5O)_3$  requires  $C = 72.18$ ;  $H = 3.75$  per cent.

Tribenzoylpurpurogallin forms minute, colourless prisms; it melts at 212—213°, and is almost insoluble in alcohol. When heated with benzoic anhydride at 180° for three hours, its melting point remained unaltered, and it thus appears that, whereas purpurogallin gives a tetra-acetyl compound, it does not yield a tetrabenzoyl derivative.

A molecular weight determination gave the following result:

0.4769 in 14.2454 naphthalene gave  $\Delta t$  0.421°.  $M = 556$ .

$C_{32}H_{20}O_8$  requires  $M = 532$ .

*Dibromopurpurogallin* was prepared by adding 1 gram of bromine to 1 gram of purpurogallin suspended in acetic acid. After remaining



The action of bromine was similar, but was even slower, and purified by Nitric acid (sp. gr. 1.2) and alkaline permanganate as the medium residue to oxalic acid.

The original black residue is obtained with the tetrabromopurpuro-alcohol, ether, and other organic substances which requires  $C=33.52$ ; general character of the

substances known as  $CO_2$  and  $0.0206 H_2O$ .  $C=35.1$ ;  $H=1.68$ .

Guthzeit (Ber., 1863)  $Br_2O_5$  requires  $C=34.92$ ;  $H=1.59$  per cent.

sacculmipotassiumpurpurogallin is best prepared by digesting acetyl-purpurogallin with boiling alcoholic potassium acetate. Without appearing to dissolve entirely, the substance is converted into a mass of minute needles which, when dry, have a purplish-brown colour. It was collected, washed with alcohol, and dried at  $160^\circ$ :

0.8732 gave 0.2877  $K_2SO_4$ .  $K=14.76$ .

1.0090 „ 0.3435  $K_2SO_4$ .  $K=15.26$ .

$C_{11}H_7O_5K$  requires  $K=15.11$  per cent.

It dissolves very sparingly in cold water, forming an orange-yellow solution and is decomposed in the boiling solvent with separation of a colouring matter having the reactions of purpurogallin. In this respect, therefore, this colouring matter differs from alizarin, the potassium salt of which is stable under these conditions.

*Purpurogallin Trimethyl Ether*.—Five grams of purpurogallin suspended in 150 c.c. of boiling methyl alcohol were mixed with excess of methyl iodide, and treated during 2 days with a solution of 10 grams of potassium hydroxide in 50 c.c. of methyl alcohol. This procedure was considered necessary in order to avoid as far as possible the oxidation of the purpurogallin. In the early stages of the reaction, it was interesting to note that the crystals of the colouring matter became transformed into a minute variety of a somewhat redder colour; this is probably the *semi-salt*,  $C_{22}H_{15}O_{10}K$ , similar to those which have been obtained from daphnetin, carminic acid, &c. (this vol., p. 129). The methylation product was evaporated to a small bulk, poured into ether, the ethereal solution well washed, evaporated, and the residue purified by crystallisation from alcohol in the presence of animal charcoal:

0.1121 gave 0.2630  $CO_2$  and 0.0545  $H_2O$ .  $C=63.98$ ;  $H=5.40$ .

$C_{11}H_5O_5(CH_3)_3$  requires  $C=64.12$ ;  $H=5.34$  per cent.

Purpurogallin trimethyl ether forms long, orange-yellow needles, sparingly soluble in alcohol. It melts at  $174-177^\circ$  and is insoluble in aqueous alkaline solutions. The average yield was about 10 per cent.

*Acetyl Derivatives.* Attempts to explain their isomerism would have little value one hydroxyl which has been further studied.

*Purpurogallin with Zinc Dust.*—Four grams of the digested it with acetic acid, the usual methods, gave a small quantity was purified by crystallisation, the semi-solid on standing overnight.

0.1160 gave 0.2686  $\text{CO}_2$  and 0.0565  $\text{H}_2\text{O}$ . Crystallised twice from  $\text{C}_{11}\text{H}_4\text{O}_5(\text{CH}_3)_3 \cdot \text{C}_2\text{H}_5\text{O}$  requires  $\text{C} = 63.15$ ;  $\text{H} = 3.30$ . Colourless leaflets,

It formed almost colourless needles melting at  $262-264^\circ$  in naphthalene, with sparingly soluble in alcohol. Slightly soluble in alcohol.

*Action of Potassium Hydroxide on Purpurogallin.*—Five g. of purpurogallin dissolved in 60 c.c. of a 50 per cent. aqueous solution of potassium hydroxide were boiled for some time in an open flask. As the liquid became more concentrated, a precipitate (probably a potassium salt of purpurogallin) gradually separated, which disappeared when the temperature had reached about  $170^\circ$ . If a solution of the product in water no longer developed a bluish-green coloration, but had a reddish tint, the melt was dissolved in much water, neutralised with acid, and extracted with ether. A brownish-yellow, crystalline substance was thus isolated, which was dissolved in boiling acetic acid and, after treatment with animal charcoal, the solution was evaporated and diluted with hot water. On standing overnight, fine, lemon-yellow needles separated, which were collected and further purified in a similar manner. The average yield was 1.3 grams.

As distinct preparations of the substance gave fairly concordant numbers on analysis ( $\text{C} = 60.88$ ;  $\text{H} = 3.07$ ;  $\text{C} = 60.81$ ;  $\text{H} = 3.18$ ), the compound appeared to be pure, but since the melting points of the acetyl derivatives obtained from these specimens did not agree, it was evident that this was not the case. Crystallisation from nitrobenzene or acetic acid did not effect a separation, but subsequently, by the employment of alcohol, two distinct substances were isolated, which it is proposed to designate as *purpurogallone* and *isopurpurogallone*. Analysis of the former gave the following result:

0.1185, dried at  $180^\circ$ , gave 0.2620  $\text{CO}_2$  and 0.0353  $\text{H}_2\text{O}$ .  $\text{C} = 60.29$ ;  $\text{H} = 3.30$ .  $\text{C}_{11}\text{H}_6\text{O}_5$  requires  $\text{C} = 60.55$ ;  $\text{H} = 2.75$  per cent.

*Purpurogallone* crystallises from alcohol in minute, yellow needles melting at  $262-264^\circ$ , and is more sparingly soluble in this solvent than *isopurpurogallone*. It is soluble in alkaline solutions with a yellow coloration, which, on exposure to air, becomes deep crimson-red; sulphuric acid dissolves it to form a greenish-yellow liquid, which nitric acid changes to orange-red. With alcoholic lead acetate, it gives a yellow precipitate, and with alcoholic ferric chloride a deep brownish-black coloration. It reacts with alcoholic potassium acetate, forming a sparingly soluble potassium salt, and dyes mordanted wool with the





properties. Attempts to explain their isomerism would have little value until the subject has been further studied.

*Distillation of Purpurogallin with Zinc Dust.*—Four grams of the colouring matter, treated by the usual methods, gave a small quantity of an oily distillate which became semi-solid on standing overnight. The product was drained on a porous tile, crystallised twice from ligroin, and finally cautiously sublimed. It formed colourless leaflets, melted at  $77-79^{\circ}$ , and had the characteristic odour of naphthalene, with which it was evidently identical. This result thus corroborates the statement of Nietzki and Steinmann (*loc. cit.*).

*Action of Alcoholic Potash on Purpurogallin Trimethyl Ether.*—The ether was digested with alcoholic potash at  $170^{\circ}$  for three hours. The product was evaporated to a small bulk, dissolved in water, the solution saturated with carbon dioxide, and shaken with ether to remove a small quantity of a viscous substance. The aqueous liquid was acidified, and from this, by means of ether, an acid was isolated which, after recrystallisation from alcohol and water, melted at  $197-199^{\circ}$ . It is soluble in aqueous alkalis, yielding colourless solutions, and is again precipitated on acidification in the form of glistening needles; with alcoholic ferric chloride, it develops a very pale olive coloration. When strongly heated, it yields a sublimate which is apparently an anhydride, for this melts at  $164-166^{\circ}$ . This acid therefore somewhat resembles *m*-hemipinic acid, and a quantity of purpurogallin trimethyl ether is being prepared in order to decide this point.

#### *Oxidation of Gallic Acid with Potassium Ferricyanide.*

As previously stated, Hooker (*loc. cit.*), by the oxidation of gallic acid with nitrous acid, obtained purpurogallin. With potassium ferricyanide and gallic acid in aqueous solution, no reaction of this nature takes place, but if some quantity of potassium or sodium acetate is present, a gentle effervescence ensues. After remaining for 24 hours, a small quantity of a precipitate had formed, and the mixture was then shaken with large volumes of ether until the extract was colourless. On evaporating off the ether, a crystalline residue remained which consisted chiefly of gallic acid, but there was present a trace of a new substance which, owing to its insolubility in cold water, could be readily isolated. As this did not lend itself to crystallisation, it was purified by washing, first with glacial acetic acid, then with ether, and finally with benzene. The yield was approximately three per cent. :

0.1158 gave 0.2299  $\text{CO}_2$  and 0.0332  $\text{H}_2\text{O}$ .  $\text{C} = 54.14$ ;  $\text{H} = 3.18$ .

0.1233 „ 0.2467  $\text{CO}_2$  „ 0.0415  $\text{H}_2\text{O}$ .  $\text{C} = 54.56$ ;  $\text{H} = 3.73$ .

$\text{C}_{11}\text{H}_7\text{O}_2 \cdot \text{CO}_2\text{H}$  requires  $\text{C} = 54.54$ ;  $\text{H} = 3.03$  per cent.

Thus obtained, the compound formed orange-red needles closely resembling those of purpurogallin itself, but somewhat smaller; it is soluble in aqueous alkalis to an orange-red solution, which, on standing in air, becomes deep blue and finally brownish-yellow. This substance does not melt below  $330^{\circ}$ , but gradually becomes darker and appears to decompose before melting; in fact, it may be said, except as regards its very sparing solubility in all the usual solvents, to be very similar in general reactions to purpurogallin itself. From the new substance, unfortunately, no well-defined derivative has yet been obtained; thus, with bromine, it is only very slowly attacked, and the product of its reaction with acetic anhydride cannot be readily crystallised. It readily dyes mordanted fabrics in shades which very closely resemble, but are somewhat redder than, those given by purpurogallin; this will be seen by the following description of the colours produced on woollen cloth:

| Chromium.      | Aluminium.    | Tin.       | Iron.           |
|----------------|---------------|------------|-----------------|
| Reddish-brown. | Reddish-puce. | Brick-red. | Brownish-black. |

There can be no doubt, therefore, that this substance is a derivative of purpurogallin, and taking into consideration its percentage, composition and formation from gallic acid, there seems every reason to presume that it is in reality a *purpurogallincarboxylic acid*.

### *Summary of Results.*

The results of this investigation indicate that the somewhat complex formula,  $C_{20}H_{16}O_9$ , is not in harmony with the molecular weight of purpurogallin, which is most probably represented as  $C_{11}H_8O_5$ . Consequently, the tetra-acetyl and tetrabromo-derivatives,  $C_{20}H_{12}O_9(C_2H_3O)_4$  and  $C_{20}H_{12}Br_4O_9$ , must be considered to be  $C_{11}H_4O_5(C_2H_3O)_4$  and  $C_{11}H_6Br_2O_5$  respectively, and it is evident that the composition of the former substance was quite inaccurately represented in regard to the percentage of acetyl groups it contained. It will be observed that purpurogallin resembles other phenolic dyestuffs (this vol., p. 129) in forming, by means of potassium acetate, the salt  $C_{11}H_7O_6K$ . Nietzki and Steinmann's discovery that naphthalene is produced by distilling purpurogallin with zinc dust has been confirmed, and although the formation of a naphthalene derivative by oxidising pyrogallol is exceedingly remarkable, the result is a strong indication that purpurogallin is derived from this hydrocarbon. If such is the case one is naturally inclined to suspect that this colouring matter contains a  $\beta$ -naphthaquinone grouping, and that the eleventh carbon atom is present in a side chain which may be an alcoholic group. The formation of a tetra-acetyl derivative is apparently against a naphthaquinone

constitution, but this cannot be regarded as certain in the light of the fact that we have as yet been unable to prepare a tetrabenzoyl compound. It is interesting to note that, whereas lapachol (Hooker, *Trans.*, 1896, 69, 1355), an  $\alpha$ -naphthaquinone derivative, contains but one hydroxyl, Paternò (*Gazzetta*, 1889, 19, 606) has described a diacetyl compound of this substance, and it is well known that at  $260^{\circ}$  in the presence of sodium acetate, benzoquinone, and acetic anhydride (Sarauw, *Annalen*, 1881, 209, 128) yield diacetylhydroquinone.

It seems possible that the purpurogallones contain respectively a carboxylic group, and that by means of acetic anhydride a lactone group is produced, but further work is necessary before it will be advisable to speculate further as regards their constitution. The investigation of the new products described in this paper is proceeding, but owing to the difficulty of preparing these in quantity, progress cannot be otherwise than slow.

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## XXI.—*The Combination of Carbon Monoxide with Chlorine under the Influence of Light.*

By GIBSON DYSON and ARTHUR HARDEN.

THE phenomenon of photochemical induction was first observed by Draper in 1843, and was more closely studied by Bunsen and Roscoe in 1857, by Pringsheim in 1887, and quite recently by Mellor and others, a mixture of hydrogen and chlorine being employed by all these chemists. It was therefore thought that the study of the action of light on a mixture of carbon monoxide and chlorine might also be of interest, particularly in view of the fact that the reaction in this case appears to be of a somewhat different chemical type from that which occurs between hydrogen and chlorine. In this case, the progress of the chemical change can, in the absence of any absorbing liquid, be measured by the contraction produced, and, moreover, it is not easy to devise any series of probable equations like those suggested by Pringsheim which shall express the combination of these two gases by the aid of an intermediate product formed during the induction



period. The experiments were commenced in 1893, and a short note was published in the *Proceedings* (1894, 10, 165) embodying some of the results obtained up to that time, and establishing the fact that a well-marked period of induction occurs in the combination of these two gases under the influence of light. This has quite recently been confirmed by Wilderman (*Proc. Roy. Soc.*, 1902, 70, 166) in an elaborate investigation on the combination of these gases.

In the present paper, a short account is given of the results obtained in the study of the first stage of the combination.

### *Experimental Details.*

Since carbon monoxide and chlorine cannot be simultaneously prepared in equivalent volumes, the method was adopted of preparing the gaseous mixture by filling two vessels of the proper volume with carbon monoxide and chlorine, and allowing the gases to mix by diffusion.

The apparatus consisted of two horizontal glass cylinders of about 108 c.c. capacity, connected with each other by a tail tap of 5/16-inch bore. One of these was connected by a similar tap with a narrow tube to serve for the introduction of various gases, and the other with the capillary limb of a U-shaped gauge, the wide limb of which had about 16 times the sectional area of the narrow limb. The gauge was provided with a tail tap at its lowest point, and the wide limb was connected with a vertical glass cylinder of 100 c.c. capacity, closed by a tap, by means of which the effect of variations in the barometric pressure was excluded. This cylinder and the horizontal cylinders were surrounded by glass jackets, through which a stream of water at a constant temperature was circulated. The gauge contained sulphuric acid, or, in some cases, carbon tetrachloride, the rate of combination of the gases being measured by the rise of the liquid in the narrow limb. Equivalence of volume between the two gases was obtained by adding the necessary amount of drawn-out glass rod to the larger cylinder. Preliminary experiments showed that the chlorine and carbon monoxide contained in the two horizontal cylinders became uniformly mixed by diffusion through the bore of the tap in about 16 hours, and in the actual experiments the gases were always allowed to diffuse for 24 hours before insolation.

*Preparation of Gases.*—The carbon monoxide was prepared by gently heating pure sodium formate with pure sulphuric acid diluted with half its volume of water, and was washed first through strong caustic potash solution, and then through two wash-bottles containing concentrated sulphuric acid. The gas was evolved at a comparatively low temperature, and was obtained so free from air that 100 c.c. when

exposed to ammoniacal cuprous chloride solution left only a minute trace of residue.

The chlorine was prepared from chlorine hydrate as described by Harker (*Zeit. physikal. Chem.*, 1892, 9, 673). The gas evolved from liquid chlorine was washed with water, and then passed into pure water kept at 4—5° by a cooling mixture and constantly shaken by mechanical means. As soon as sufficient chlorine hydrate had been formed, the bottle containing it was placed in warm water, the tap on the supply tube closed, and the delivery tube connected by a ground-glass joint with a sealed system of two wash-bottles containing concentrated sulphuric acid. The gas was then delivered to the insolation apparatus by means of a plane-faced glass joint. The chlorine, therefore, after its transformation into hydrate, only came into contact with water, sulphuric acid, and glass, and the whole operation was carried out in a darkened room.

One cylinder of the insolation apparatus was first filled with carbon monoxide at the temperature of the water-jacket and under the atmospheric pressure by passing a slow stream of the gas for 3 hours, and the second cylinder was then filled with chlorine under similar conditions, the apparatus being in this case supported in a vertical position.

*The Period of Induction.*—When the mixed gases are exposed to light the combination between them exhibits a well-marked period of induction, the rate of combination increasing gradually to a maximum. The induced gases, when subsequently placed in the dark, pass more or less completely into the non-induced condition, so that, on re-exposure to light, a second period of induction is observed.

Although these phenomena were invariably noticed, it was found impossible to obtain mixtures of the gases on successive occasions which showed exactly the same period of induction or the same final sensitiveness to light.

The source of light employed in these experiments was the outer ring of a 50-candle Argand gas burner, supplied with gas through a Moitessier pressure regulator, the flame being kept at a constant height, and placed at 54.7 cm. from the insolation apparatus. The typical course of the experiment was that no change occurred at first; and then, after the lapse of a varying period, which sometimes amounted to more than half an hour, the liquid in the gauge began to rise slowly, without any preliminary dip, the rate of this rise gradually increasing, and finally becoming practically constant. When the light was shut off, the contraction continued for a short interval, and then ceased entirely. If the gas were then at once re-exposed to the light, the recommencement of the action was marked by an expansion. Both this expansion and the contraction which occurs after the extinction of

the light appear to be due to the imperfect cooling of the gases by the water-jacket, the temperature of the mixture being slightly raised by the heat evolved on combination. Both these phenomena are intensified when the mixed gases are illuminated by a more powerful light, such as that from burning magnesium ribbon or diffused daylight; they are probably due entirely to the heat produced by the combination, and are not in any way specially characteristic of reactions induced by illumination, as was supposed by Recklinghausen (*Zeit. physikal. Chem.*, 1894, 14, 491).

The following table illustrates the phenomena of induction (A), and re-induction after 13 hours (B). The numbers represent the rise of sulphuric acid in the gauge during successive periods of 5 minutes. It will be observed that the lapse of induction is by no means complete, the second period of induction being much shorter than the first:

| Exposure in minutes ... | 5   | 10  | 15 | 20 | 25 | 30 | 35  | 40  | 45  | 50   | 55   | 60 | 65 | 70   |
|-------------------------|-----|-----|----|----|----|----|-----|-----|-----|------|------|----|----|------|
| A .....                 | 0   | 0   | 0  | 0  | 0  | 0  | 0.8 | 1.3 | 9.9 | 20.5 | 24.8 | 28 | 31 | 37.7 |
| B .....                 | 1.9 | 4.6 | 12 | 37 | —  | —  | —   | —   | —   | —    | —    | —  | —  | —    |

*Effect of Admixed Gases.*—In order to ascertain the effect produced on the reaction by an excess of one of the constituents of the mixture, or any other gas, the gas in question was passed into the narrow tube connected with the horizontal cylinders and allowed to mix with the carbon monoxide and chlorine by diffusion. The capacity of this portion of the apparatus was 13.2 c.c., so that the resulting mixture contained 5.65 per cent. of the added gas.

Carbon tetrachloride and water vapour were introduced by saturating one of the gases with the vapour of the liquid, so that the resulting mixture was half saturated.

The addition of air was found to have a definite specific effect on the reaction, but the other gases did not produce any greater difference than could be observed between separate experiments with the normal mixture.

In the table on p. 205, the numbers represent the rise in mm. of sulphuric acid in the gauge during 5 minutes' exposure.

The saturation of one of the gases with water vapour at 10° produced no marked change in the course of the reaction.

The combination of the gases takes place on exposure to a bright light even when the mixture has been dried for a long time over phosphoric anhydride. One sample was collected over sulphuric acid, sealed up in a tube containing phosphoric anhydride, and then preserved



| Exposure in minutes. | Gas added.         |                  |                    |                        |      |
|----------------------|--------------------|------------------|--------------------|------------------------|------|
|                      | Carbonyl chloride. | Carbon monoxide. | Hydrogen chloride. | Carbon tetra-chloride. | Air. |
| 5                    | 2                  | 0                | 0                  | 0                      | 0    |
| 10                   | 9.2                | 0                | 0                  | 0                      | 0.5  |
| 15                   | 12.8               | 0                | 1.3                | 0                      | 0.7  |
| 20                   | 12.8               | 0                | 6.7                | 0                      | 1.2  |
| 25                   | 13.8               | 3.6              | 8.9                | 0.9                    | 2.3  |
| 30                   | 15.2               | 15.1             | 8.1                | 10                     | 1.8  |
| 35                   | 15.3               | 20.1             | 8.2                | 17                     | 2.5  |
| 40                   | —                  | 20.7             | 9.7                | 19.2                   | 3.6  |
| 45                   | —                  | —                | 9.9                | 19.8                   | 2.4  |
| 50                   | —                  | —                | 11                 | 22.3                   | 2.5  |
| 55                   | —                  | —                | —                  | —                      | 2.5  |

for a month in the dark. On exposure to light, combination occurred, accompanied by the usual diminution of pressure and formation of carbonyl chloride.

#### *Summary of Experimental Results.*

1. When a mixture of carbon monoxide with chlorine, dried by being passed through sulphuric acid, is exposed to light, a well-marked period of photochemical induction occurs.

2. The effect of induction slowly disappears when the exposed gas is placed in the dark.

3. The period of photochemical induction is greatly diminished by an admixture of air, but does not appear to be specifically affected by the presence of carbonyl chloride, hydrogen chloride, excess of carbon monoxide, carbon tetrachloride vapour, and small amounts of water vapour.

The fact that a mixture of carbon monoxide and chlorine behaves towards light in an analogous manner to one of hydrogen and chlorine seems to furnish evidence in favour of the hypothesis that light acts specifically on chlorine in the presence of a gas with which it can combine. It is not yet certain whether, under these circumstances, this action leads to the transference of energy to the chlorine molecule in such a way as to set up characteristic vibrations, or whether it brings about the formation of a chemical compound which acts as a carrier between the two combining gases.

Any explanation offered should, however, be capable of application to the case of carbon monoxide and chlorine as well as to that of hydrogen and chlorine, since the phenomena common to the two reactions appear to be due to the same cause.

XXII.—*The Rate of Decomposition of Diazo compounds. Part II. Diazo-compounds of the Naphthalene Series.*

By JOHN CANNELL CAIN and FRANK NICOLL.

IN our investigation of the rate of decomposition of diazo-salts by water, it has been shown (Trans., 1902, 81, 1412) that a number of these compounds belonging to the benzene series decompose in accordance with the well-known expression

$$\frac{1}{t} \log \frac{A}{A-x} = C \text{ (a constant).}$$

We have now extended our experiments to members of the naphthalene series and the results are described in this paper.

So far as we know the rate of decomposition of the diazo-salts of the naphthalene series has not been determined, although the reaction itself is carried out on the large scale, for instance, in the manufacture of  $\alpha$ -naphthol-4-sulphonic acid from naphthionic acid.

We have measured the rate of decomposition by water of the diazo-salts prepared from the following amines:—

$\alpha$ -Naphthylamine and its monosulphonic acids, [ $\text{NH}_2 = 1 : \text{SO}_3\text{H} = 2, 4, 5, \text{ and } 8$ ],  $\beta$ -naphthylamine, its monosulphonic acids, [ $\text{NH}_2 = 2 : \text{SO}_3\text{H} = 6 \text{ and } 7$ ], and disulphonic acids, [ $\text{NH}_2 = 2 : 2\text{SO}_3\text{H} = 3 : 6, \text{ and } 6 : 8$ ], 7-amino- $\alpha$ -naphthol-3-sulphonic acid, and 8-amino- $\alpha$ -naphthol-3 : 6-disulphonic acid.

The method and apparatus used to measure the rate of decomposition were exactly the same as those fully described in our first paper (*loc. cit.*).

The naphthols and their sulphonic acids exhibit a greater capacity for coupling with diazo-compounds than the phenols of the benzene series, and accordingly, whenever combination is possible, the decomposition of the diazonaphthalene derivatives is complicated by the formation of an azo-compound. In the benzene series, on the other hand, no such secondary reaction was observed in the case of those substances which formed the subject of our first paper.

It might be expected, in view of the greater reactivity of the naphthols as contrasted with the benzenoid phenols, that, after a certain amount of the diazo-salt had decomposed, the naphthol thus produced would condense with a portion of the undecomposed diazo-compound even in the mineral acid solution.

Such a formation of an azo-colouring matter is theoretically possible in all the above cases with the exception of  $\alpha$ -naphthylamine-8-sulphonic acid, the diazo-salt of which does not yield  $\alpha$ -naphthol-8-sulph-

onic acid but the corresponding insoluble sultone, and  $\beta$ -naphthylamine-6:8-disulphonic acid, which gives a naphtholdisulphonic acid combining with only a few very reactive diazo-salts.

In those cases where the diazo-salt remains in solution, we have calculated out the values of  $C$  according to the formula

$$\frac{1}{t} \log \frac{A}{A-x} = C,$$

and the constant values obtained for  $C$  show that the reaction is a unimolecular one up to a certain point.

Theoretically, it would seem probable that, as soon as a small portion of the hydroxy-compound is formed, it should immediately combine with some of the diazo-salt, thus destroying at once the unimolecular character of the reaction. But we have found that the hydroxy-compound formed does not combine with the diazo-salt until a definite quantity of the former has been produced. Further, the quantity of hydroxy-compound which must be formed (or the amount of diazo-salt which must be decomposed) before combination takes place is different in each case. The point at which the formation of azo-compound begins, is easily seen by the change in the colour of the solution, and, moreover, the values of  $C$ , which have been constant up to this stage, now begin to decrease rapidly.

A comparison may even be made between the combining or "coupling" powers of the various naphthols, for one would expect that the production of a reactive naphthol would cause the constancy of  $C$  to disappear more rapidly than if the hydroxy-compound condensed with less readiness.

The diazo-solutions derived from the naphthylamines behave differently, because  $\alpha$ -naphthol "couples" much more readily than its isomeride. A similar contrast is noticed in the case of the diazotised  $\beta$ -naphthylaminedisulphonic acids, the "G" acid,  $[\text{NH}_2:2\text{SO}_3\text{H} = 2:6:8]$ , forming no colouring matter, whereas the "R" acid,  $[\text{NH}_2:2\text{SO}_3\text{H} = 2:3:6]$ , yields an azo-derivative when 50 per cent. of the diazo-compound has been decomposed; this result accords with the well-known difference in the "coupling" powers of the corresponding naphtholdisulphonic acids.

In studying the decomposition of those diazo-derivatives which are insoluble in water, we cannot, of course, apply the above formula, as the active mass is not equal to the quantity of diazo-compound present.

It must also be remembered that these diazo-derivatives are anhydrides, so that the compound,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N:N} \\ \text{SO}_2 \end{smallmatrix} \text{O}$ , momentarily forms an intermediate soluble substance before evolution of nitrogen takes place.



The rate of decomposition of these compounds is expressed by the simple formula

$$\frac{x}{t} = K \text{ (a constant),}$$

$x$  being the observed volume of nitrogen evolved in the time  $t$  (in minutes) as before.

The secondary reaction, leading to the formation of an azo-colouring matter, also interferes, whenever possible, with the simple decomposition of these insoluble diazo-compounds; its commencement is again clearly shown by the diminution in the values of  $K$ .

### 1. *$\alpha$ -Diazonaphthalene Chloride.*

An ice-cold solution of 14.3 grams of  $\alpha$ -naphthylamine (1/10 mol.) in 30 c.c. of hydrochloric acid of sp. gr. 1.16 (3/10 mol.), was treated with an aqueous solution containing 6.9 grams of sodium nitrite and the diazo-solution made up to 1400 c.c. so that it contained 13.6 grams of diazo-chloride in a litre.

This diazo-solution is exactly equivalent to and comparable with the solution of diazobenzene chloride used in our first paper.

Thirty-five c.c. were taken in each experiment.

*Temperature 60°.*

$A = 60.4$  c.c. (16°, 757 mm.).

| $t.$ | $x.$     | $C.$   |
|------|----------|--------|
| 3    | 7.8 c.c. | 0.0200 |
| 4    | 10.1 "   | 0.0199 |
| 5    | 12.5 "   | 0.0201 |
| 6    | 14.8 "   | 0.0203 |
| 8    | 18.8 "   | 0.0202 |
| 9    | 20.3 "   | 0.0197 |
| 10   | 21.7 "   | 0.0193 |
| 14   | 25.6 "   | 0.0171 |
| 20   | 29.0 "   | 0.0142 |
| 40   | 33.9 "   | 0.0089 |
| 60   | 35.3 "   | 0.0063 |
| 180  | 39.5 "   | 0.0025 |

Mean 0.020.

Azo-compound formed.

The value of  $C$  thus remains constant up to a certain point ( $x = 20$  c.c.), or until 33 per cent. of the diazo-salt has been decomposed.

At this point, a second reaction begins, namely, the formation of the red colouring matter,  $\alpha$ -naphthaleneazo- $\alpha$ -naphthol, so that the

two reactions go on simultaneously. The rapid diminution in the value of the constant shows that the rate of formation of this azo-compound increases as the quantity of  $\alpha$ -naphthol becomes greater.\* The point at which this secondary reaction commences depends on the amount of free acid present in the solution: by increasing the quantity of hydrochloric acid the formation of the azo-compound would begin at a later stage owing to the well-known "hindering" effect of this reagent.

## 2. $\beta$ -Diazonaphthalene Chloride.

A solution of 14.3 grams of  $\beta$ -naphthylamine in 10 c.c. of hydrochloric acid of sp. gr. 1.16 was diluted to 500 c.c. Of this solution, 12.5 c.c. were diazotised with 0.5 c.c. of hydrochloric acid and 0.173 gram of sodium nitrite dissolved in water, the diazo-solution being then diluted to 35 c.c. in order that the concentration should be equal to that in the previous case.

Temperature 60°.

$A = 61.3$  c.c. (19°, 756 mm.).

| $t.$ | $x.$      | $C.$   |
|------|-----------|--------|
| 5    | 15.1 c.c. | 0.0246 |
| 6    | 18.0 "    | 0.0251 |
| 8    | 22.8 "    | 0.0252 |
| 10   | 26.8 "    | 0.0250 |
| 11   | 28.6 "    | 0.0248 |
| 12   | 30.1 "    | 0.0244 |
| 14   | 32.7 "    | 0.0237 |
| 18   | 36.1 "    | 0.0214 |
| 23   | 38.6 "    | 0.0188 |
| 30   | 40.2 "    | 0.0154 |
| 62   | 42.8 "    | 0.0084 |

Mean 0.025.

Azo-compound formed.

Here again the decomposition obeys the law, and  $\beta$ -naphthalene-azo- $\beta$ -naphthol is formed when about 50 per cent. of the diazo-salt has been decomposed.

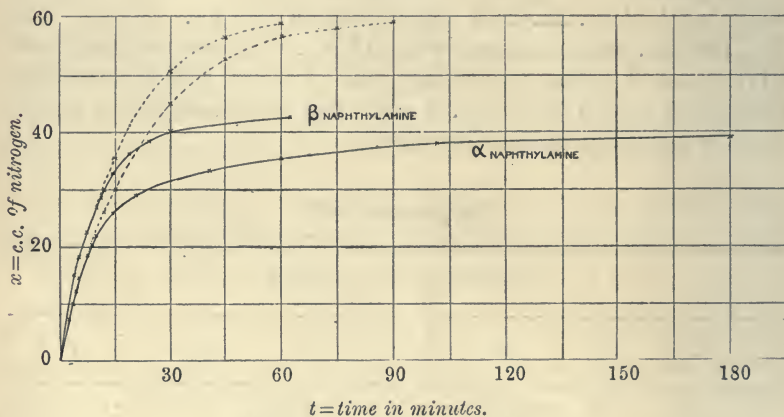
Comparing the values of  $C$  for the "constant" periods in these two cases, it is seen that the diazo-salt from  $\alpha$ -naphthylamine ( $C = 0.020$ ) is more stable than that from  $\beta$ -naphthylamine ( $C = 0.025$ ).

\* See Goldschmidt, "Dynamische Untersuchungen über die Bildung der Azo-farbstoffe" (*Ber.*, 1897, **30**, 670, 2075; 1899, **32**, 355; 1900, **33**, 893; 1902, **35**, 3534).

The curves in Fig. 1, obtained by taking corresponding values of  $x$  and  $t$  as ordinates and abscissæ respectively, illustrate this difference in the stability of the two diazo-salts, and also indicate that the formation of the azo-compound commences sooner in the case of the  $\alpha$ -compound than in that of its  $\beta$ -isomeride. The dotted lines represent the relationships which would exist between  $x$  and  $t$ , providing that the reactions are unimolecular throughout.

These curves do not furnish an exact comparison, because the values of  $A$  differed in the two experiments, but the difference is negligible.

CURVE 1.



### 3. $\alpha$ -Diazonaphthalene-2-sulphonic Acid.

An aqueous solution containing 0.6125 gram of sodium  $\alpha$ -naphthylamine-2-sulphonate was diazotised with 1 c.c. of hydrochloric acid of sp. gr. 1.16, and 0.173 gram of sodium nitrite also dissolved in water, the whole being diluted to 35 c.c. The greater portion of the diazo-compound separated out, being almost insoluble in this solution.



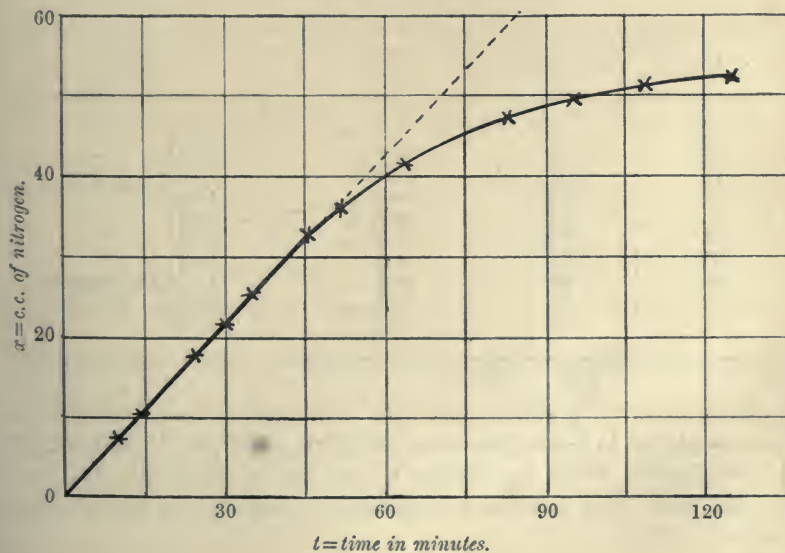
| Temperature 70°.                |          |       | Temperature 80°.                |          |       |
|---------------------------------|----------|-------|---------------------------------|----------|-------|
| $A = 60.9$ c.c. (17°, 754 mm.). |          |       | $A = 60.9$ c.c. (17°, 754 mm.). |          |       |
| $t$ .                           | $x$ .    | $K$ . | $t$ .                           | $x$ .    | $K$ . |
| 10                              | 7.6 c.c. | 0.76  | 2                               | 7.4 c.c. | 3.7   |
| 14                              | 10.5 "   | 0.75  | 3                               | 10.8 "   | 3.6   |
| 25                              | 17.7 "   | 0.71  | 4                               | 14.4 "   | 3.6   |
| 30                              | 21.7 "   | 0.72  | 5                               | 17.8 "   | 3.6   |
| 35                              | 25.4 "   | 0.73  |                                 |          |       |
| 46                              | 32.7 "   | 0.71  |                                 |          |       |
| 52                              | 36.0 "   | 0.69  |                                 |          |       |
| 64                              | 41.4 "   | 0.65  |                                 |          |       |
| 83                              | 47.2 "   | 0.57  |                                 |          |       |
| 95                              | 49.7 "   | 0.52  |                                 |          |       |
| 108                             | 51.2 "   | 0.47  |                                 |          |       |
| 125                             | 52.2 "   | 0.42  |                                 |          |       |

We were unable to continue the experiment at 80°, beyond the point shown by the figures, owing to excessive foaming in the flask.

The value of  $K$  is calculated from the equation  $\frac{x}{t} = K$ .

The results obtained at 70° show that during the first period the decomposition obeys this law, and the diminishing values of  $K$  indicate

CURVE 2.



the second period, during which,  $\alpha$ -naphthalene-4-azo- $\alpha$ -naphthol-2:2'-disulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$ , is formed.

This azo-compound, which does not seem to have been described, has a blue colour and forms a brownish-yellow sodium salt.

The curve (Fig. 2, p. 211) showing the course of the reaction at  $70^\circ$  is rectilinear at first as required by the above equation, and the latter curvilinear portion indicates the period of formation of the azo-compound.

#### 4. $\alpha$ -Diazonaphthalene-4-sulphonic Acid.

This diazo-compound was prepared from sodium  $\alpha$ -naphthylamine-4-sulphonate (sodium naphthionate) exactly as in the preceding case.

The diazo-compound is very sparingly soluble in water, but slightly more soluble than the preceding one. An examination of the curve (Fig. 3, p. 213) will show that there is an appreciable error at the beginning of the reaction. This error increases with the solubility of the diazo-compound; a correction is however easily obtained by producing the straight line backwards till it cuts the zero ordinate. This point is now taken as the origin.

Temperature  $80^\circ$ .

$A = 60.5$  c.c. ( $16.5^\circ$ , 757 mm.)

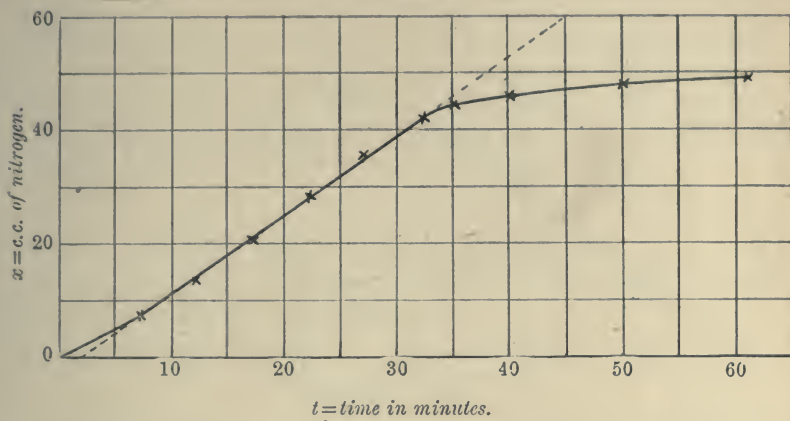
| $t$ . | $t$ corrected. | $x$ .    | $K$ . |
|-------|----------------|----------|-------|
| 7     | 5              | 7.6 c.c. | 1.52  |
| 12    | 10             | 13.8 "   | 1.38  |
| 17    | 15             | 21.0 "   | 1.40  |
| 22    | 20             | 28.5 "   | 1.42  |
| 27    | 25             | 35.9 "   | 1.43  |
| 32    | 30             | 42.6 "   | 1.42  |
| 35    | 33             | 44.5 "   | 1.35  |
| 40    | 38             | 46.2 "   | 1.21  |
| 50    | 48             | 48.1 "   | 1.00  |
| 61    | 59             | 49.2 "   | 0.83  |

Mean 1.43

Azo-compound  
formed

Here, as in the preceding case, the azo-compound,  $\alpha$ -naphthalene-2-azo- $\alpha$ -naphthol-4:4'-disulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$ , is not formed until a considerable amount of diazo-salt has been decomposed. The reaction is graphically represented by the following curve:

CURVE 3

5.  $\alpha$ -Diazonaphthalene-5-sulphonic Acid.

The diazo-compound, prepared in the ordinary way from sodium  $\alpha$ -naphthylamine-5-sulphonate, is almost insoluble in water.

Temperature 70°.

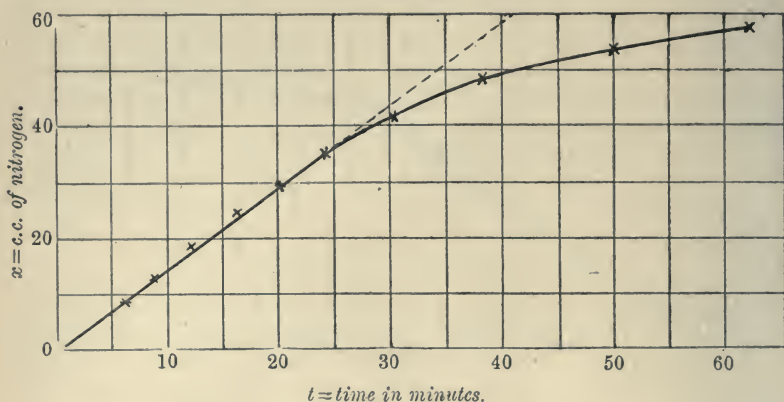
$A = 60.6$  c.c. (17°, 757 mm.).

| <i>t.</i> | <i>x.</i> | <i>K.</i> |
|-----------|-----------|-----------|
| 6         | 8.5 c.c.  | 1.42      |
| 8.5       | 12.7 „    | 1.49      |
| 12        | 18.3 „    | 1.52      |
| 16        | 24.2 „    | 1.51      |
| 20        | 29.8 „    | 1.49      |
| 24        | 35.1 „    | 1.46      |
| 30        | 41.5 „    | 1.38      |
| 38        | 48.1 „    | 1.26      |
| 50        | 53.0 „    | 1.06      |
| 62        | 55.0 „    | 0.88      |

Here again, after a "constant" period, a small quantity of  $\alpha$ -naphthalene 2-azo- $\alpha$ -naphthol-5:5'-disulphonic acid is formed :



CURVE 4.

6. *α-Diazonaphthalene-8-sulphonic Acid.*

The diazo-compound, prepared from sodium *α*-naphthylamine-8-sulphonate exactly as in the preceding experiments, is soluble in water. As the decomposition product is not *α*-naphthol-8-sulphonic acid, but the corresponding sultone,  $C_{10}H_6 \begin{matrix} O(1) \\ \diagdown \\ SO_2(8) \end{matrix}$ , no colouring matter can be formed in this case and the decomposition is throughout in accordance with the equation  $\frac{1}{t} \log \frac{A}{A-x} = C$ .

Temperature 60°.

$$A = 60.5 \text{ (16°, 755 mm.)}.$$

| t. | x.       | C.     |
|----|----------|--------|
| 6  | 8.0 c.c. | 0.0103 |
| 8  | 10.1 "   | 0.0099 |
| 13 | 16.1 "   | 0.0103 |
| 18 | 21.4 "   | 0.0105 |
| 23 | 26.1 "   | 0.0107 |
| 28 | 29.8 "   | 0.0105 |
| 36 | 35.2 "   | 0.0105 |
| 43 | 38.7 "   | 0.0103 |
| 49 | 41.7 "   | 0.0104 |
| 59 | 44.9 "   | 0.0100 |

Range 13 to 74 per cent. Mean 0.01034.

The reaction is thus unimolecular, the sultone formed separating out at once.

Comparing this value of  $C$  with that for  $\alpha$ -diazonaphthalene chloride (0.02), we see that, as was to be expected, the presence of the sulphonic group greatly increases the stability of the molecule. This influence was also noticed on comparing the diazo-derivatives of aniline and sulphanilic acid in the former communication (*loc. cit.*).

### 7. $\beta$ -Diazonaphthalene-6-sulphonic Acid.

The diazo-solution was prepared from sodium  $\beta$ -naphthylamine-6-sulphonate as in the previous example.

Temperature 60°.

$A = 61.7$  c.c. (20°, 755 mm.).

| $t$ . | $x$ .     | $C$ .  |
|-------|-----------|--------|
| 12    | 16.3 c.c. | 0.0111 |
| 14    | 18.7 "    | 0.0112 |
| 17    | 22.5 "    | 0.0116 |
| 20    | 25.8 "    | 0.0118 |
| 24    | 29.6 "    | 0.0118 |
| 27    | 32.3 "    | 0.0119 |
| 30    | 34.8 "    | 0.0120 |
| 33    | 36.7 "    | 0.0119 |
| 36    | 39.0 "    | 0.0121 |
| 43    | 43.0 "    | 0.0121 |
| 54    | 47.1 "    | 0.0116 |
| 60    | 48.4 "    | 0.0111 |
| 80    | 50.2 "    | 0.0091 |

Mean 0.0117

The decomposition is therefore unimolecular until 80 per cent. of the diazoanhydride is decomposed, then the value of  $C$  is no longer constant and the red azo-compound,  $\beta$ -naphthalene-azo- $\beta$ -naphthol-6:6'-disulphonic acid, is formed.

### 8. $\beta$ -Diazonaphthalene-7-sulphonic Acid.

The diazo-compound was prepared from sodium  $\beta$ -naphthylamine-7-sulphonate.

*Temperature 60°.*

| I. $A=61.1$ c.c. ( $18^\circ$ , 755 mm.). |           |           | II. $A=61.5$ c.c. ( $16.5^\circ$ , 745 mm.). |           |           |
|---|-----------|-----------|--|-----------|-----------|
| <i>t.</i>                                 | <i>x.</i> | <i>C.</i> | <i>t.</i>                                    | <i>x.</i> | <i>C.</i> |
| 14  | 17.0 c.c. | 0.0101    | 14   | 16.7 c.c. | 0.0098    |
| 16  | 19.3 "    | 0.0103    | 16   | 18.9 "    | 0.0100    |
| 18  | 21.3 "    | 0.0103    | 20   | 22.8 "    | 0.0100    |
| 25  | 27.3 "    | 0.0103    | 30   | 31.3 "    | 0.0103    |
| 30  | 31.1 "    | 0.0103    | 36   | 34.8 "    | 0.0101    |
| 38  | 36.0 "    | 0.0102    | 44.5   | 39.1 "    | 0.0099    |
| 45  | 39.4 "    | 0.0100    | 57   | 44.0 "    | 0.0096    |
| 55  | 43.3 "    | 0.0097    | 80   | 48.7 "    | 0.0085    |
| 70  | 47.2 "    | 0.0092    | 123  | 51.9 "    | 0.0065    |
| 86  | 48.8 "    | 0.0081    |  |           |           |

Mean 0.0102

Mean 0.0100

Azo-  
compound  
formedAzo-  
compound  
formed

The reaction is unimolecular until about 65 per cent. of the diazo-anhydride has decomposed; after this the formation of azo-compound begins. The stability of this diazoanhydride is only very slightly greater than that of the preceding isomeride, but both diazo-compounds are much more stable than  $\beta$ -diazonaphthalene chloride.

#### 9. $\beta$ -Diazonaphthalene-6:8-disulphonic Acid.

A neutral solution, prepared by dissolving 0.8525 gram of potassium hydrogen  $\beta$ -naphthylamine 6:8-disulphonate in the requisite amount of aqueous caustic soda, was diazotised with  $1\frac{1}{4}$  c.c. of hydrochloric acid and 0.173 gram of sodium nitrite and then diluted to 35 c.c.



*Temperature 60°.*

| 1.<br><i>A</i> = 60.5 c.c. (16°, 755 mm.). |           |           | 2.<br><i>A</i> = 60.8 c.c. (17°, 755 mm.). |           |           |
|--|-----------|-----------|--|-----------|-----------|
| <i>t.</i>                                  | <i>x.</i> | <i>C.</i> | <i>t.</i>                                  | <i>x.</i> | <i>C.</i> |
| 25   | 16.0 c.c. | 0.00534   | 35   | 21.2 c.c. | 0.00532   |
| 30   | 18.9 "    | 0.00542   | 40   | 23.9 "    | 0.00542   |
| 36   | 22.0 "    | 0.00545   | 45   | 26.0 "    | 0.00538   |
| 42   | 24.9 "    | 0.00549   | 52   | 29.0 "    | 0.00541   |
| 50   | 28.4 "    | 0.00551   | 60   | 31.7 "    | 0.00533   |
| 56   | 30.2 "    | 0.00536   | 70   | 35.1 "    | 0.00534   |
| 60   | 31.9 "    | 0.00542   | 80   | 38.2 "    | 0.00537   |
| 70   | 35.3 "    | 0.00543   | 90   | 40.7 "    | 0.00534   |
| 80   | 38.4 "    | 0.00547   |  |           |           |
| 90   | 40.8 "    | 0.00541   |  |           |           |
| 100  | 42.9 "    | 0.00526   |  |           |           |
| 110  | 44.8 "    | 0.00533   |  |           |           |
| Range 26 to 74 per cent. Mean 0.00541      |           |           | Range 35 to 67 per cent. Mean 0.00536      |           |           |

Mean of the two experiments, 0.00539.

The reaction is unimolecular throughout, and no azo-compound is produced.

10. *β-Diazonaphthalene-3:6-disulphonic Acid.*

The diazo-solution was prepared from 0.8125 gram of sodium hydrogen *β*-naphthylamine-3:6-disulphonate as in the case of the preceding compound.

*Temperature 60°.*

| <i>A</i> = 60.5 c.c. (16°, 755 mm.). |           |                     |
|--------------------------------------|-----------|---------------------|
| <i>t.</i>                            | <i>x.</i> | <i>C.</i>           |
| 40                                   | 8.8 c.c.  | 0.00171             |
| 60                                   | 12.9 "    | 0.00173             |
| 80                                   | 16.6 "    | 0.00174             |
| 112                                  | 21.8 "    | 0.00173             |
| 140                                  | 25.2 "    | 0.00167             |
| 160                                  | 27.3 "    | 0.00163             |
| 171                                  | 28.5 "    | 0.00162             |
| 193                                  | 31.5 "    | 0.00165             |
| 220                                  | 33.7 "    | 0.00161             |
| 240                                  | 35.3 "    | 0.00158             |
| 359                                  | 43.0 "    | 0.00150             |
|                                      |           | Mean 0.00168        |
|                                      |           | Azo-compound formed |

The reaction is unimolecular until 50 per cent. of the diazoanhydride is decomposed, when a red azo-compound begins to be formed.

11. 8-Hydroxy- $\beta$ -diazonaphthalene-6-sulphonic Acid.

A solution of 0.5975 gram of 7-amino- $\alpha$ -naphthol-3-sulphonic acid in aqueous caustic soda (0.1 gram NaOH) is treated with  $1\frac{1}{4}$  c.c. of hydrochloric acid of sp. gr. 1.16 and 0.173 gram of sodium nitrite, the mixture being then diluted to 35 c.c. The diazo-salt is yellow and sparingly soluble.

Temperature 80°.

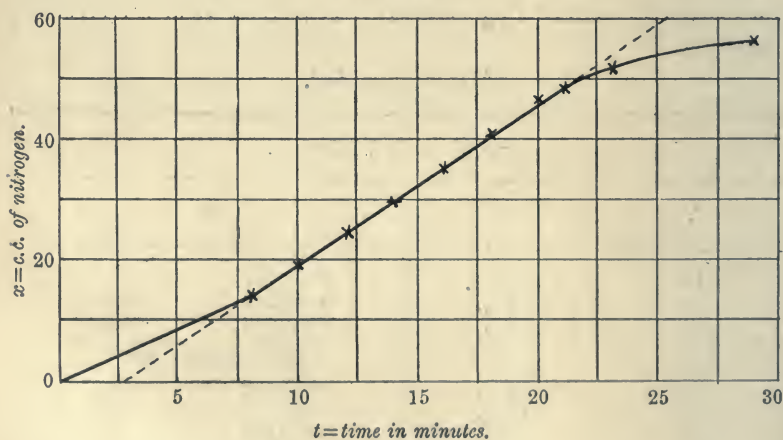
$A = 60.7$  c.c. (14.8°, 748 mm.).

| $t$ . | $t$ (corrected). | $x$ .     | $K$ . |
|-------|------------------|-----------|-------|
| 8     | 5.4              | 14.5 c.c. | 2.68  |
| 10    | 7.4              | 19.6 "    | 2.65  |
| 12    | 9.4              | 24.7 "    | 2.63  |
| 14    | 11.4             | 29.9 "    | 2.62  |
| 16    | 13.4             | 35.4 "    | 2.64  |
| 18    | 15.4             | 41.2 "    | 2.67  |
| 20    | 17.4             | 46.9 "    | 2.69  |
| 21    | 18.4             | 48.7 "    | 2.64  |
| 23    | 20.4             | 52.0 "    | 2.55  |
| 29.5  | 27.1             | 56.7 "    | 2.09  |

Mean 2.65

Azo-compound  
formed

CURVE 5.



On reference to the curve (Fig. 5) it is seen that the error of experiment at the beginning is sufficiently large to prevent us obtaining

constant values for  $K$  until 24 per cent. of the nitrogen has been evolved, and then the reaction obeys the law for insoluble diazo-compounds, but when the decomposition reaches 80 per cent. this agreement is again destroyed, owing to the formation of an azo-compound. By subtracting 2.6 from the observed values of  $t$ , we obtain the necessary correction.

12. 8-Hydroxy- $\alpha$ -diazonaphthalene-3:6-disulphonic Acid.

The diazo-solution was prepared by neutralising 0.8125 gram of the sodium hydrogen 8-amino- $\alpha$ -naphthol-3:6-disulphonate, with aqueous caustic soda, and adding 1.75 c.c. of hydrochloric acid and 0.173 gram of sodium nitrite.

Temperature 80°.

| I.                              |           |        | II.                             |           |        |
|---------------------------------|-----------|--------|---------------------------------|-----------|--------|
| $A=60.6$ c.c. (14.5°, 748 mm.). |           |        | $A=60.6$ c.c. (14.5°, 748 mm.). |           |        |
| $t$ .                           | $x$ .     | $C$ .  | $t$ .                           | $x$ .     | $C$ .  |
| 16                              | 21.5 c.c. | 0.0119 | 14                              | 19.1 c.c. | 0.0117 |
| 18                              | 23.8 "    | 0.0120 | 18                              | 23.2 "    | 0.0116 |
| 20                              | 25.9 "    | 0.0121 | 20                              | 25.3 "    | 0.0117 |
| 24                              | 29.6 "    | 0.0121 | 22                              | 27.5 "    | 0.0119 |
| 28                              | 32.8 "    | 0.0121 | 24                              | 29.4 "    | 0.0120 |
| 30                              | 34.5 "    | 0.0122 | 30                              | 34.3 "    | 0.0121 |
| 34                              | 37.2 "    | 0.0122 | 34                              | 36.9 "    | 0.0120 |
| 40                              | 40.8 "    | 0.0121 | 36                              | 38.1 "    | 0.0120 |
| 45                              | 43.3 "    | 0.0121 | 40                              | 40.3 "    | 0.0119 |
| 50                              | 45.3 "    | 0.0120 | 44                              | 42.3 "    | 0.0118 |
| 90                              | 48.3 "    | 0.0077 | 90                              | 48.1 "    | 0.0076 |
| Mean 0.0121                     |           |        | Mean 0.0119                     |           |        |
| Azo-compound formed             |           |        | Azo-compound formed             |           |        |

Mean of the two experiments, 0.0120. ....

The reaction is thus unimolecular until about 70 per cent. of the substance is decomposed, and then the bluish-red azo-colouring matter is formed.

The above diazo-salts resolve themselves into two classes: the one, containing those which are soluble and decompose according to the logarithmic law, until an azo-compound is formed; and the other, including the insoluble diazo-compounds which we have shown to decompose according to the equation  $\frac{x}{t} = K$ . Considering, first of all, the diazo-salts belonging to this latter class, we may arrange our results as follows:



| Diazo-salts from                                  | Temperature. | <i>K</i> . | Relative rate of decomposition. |
|---|--------------|------------|---------------------------------|
| $\alpha$ -Naphthylamine-2-sulphonic acid.....     | 70°          | 0.72       | —                               |
| $\alpha$ -Naphthylamine-4-sulphonic " ".....      | 80           | 3.6        | 2.3                             |
| $\alpha$ -Naphthylamine-5-sulphonic " ".....      | 80           | 1.24       | 1                               |
| $\alpha$ -Naphthylamine-3-sulphonic " ".....      | 70           | 1.48       | 6                               |
| 7-Amino- $\alpha$ -naphthol-3-sulphonic acid..... | 80           | 2.65       | 2.1                             |

The fourth column, which indicates the relative rate of decomposition, is obtained by assuming that the ratio of the values of *K* at 70° and 80° is the same for all the above substances; this assumption was shown to be justifiable in the case of the compounds studied in the previous communication (*loc. cit.*).

Thus the diazo-compound from the 1:4-acid is the most, and that from the 1:5-acid the least, stable. We cannot, of course, compare the stability of the above insoluble diazo-compounds with that of any of the soluble diazo-salts, as the course of the reaction is so different in the two cases.

As the experiments performed on the soluble diazo-compounds were carried out at 60°, excepting those with diazotised 8-amino- $\alpha$ -naphthol-3:6-disulphonic acid, the results are strictly comparable, not only among themselves, but also with those obtained from diazobenzene chloride at the same temperature. This comparison is indicated in the following table:

| Diazo-salts from                                 | <i>C</i> . | Relative rate of decomposition. | Remarks.   |
|--|------------|---------------------------------|--|
| Aniline .....                                    | 0.109      | 64.9                            |  |
| $\alpha$ -Naphthylamine .....                    | 0.020      | 11.9                            | { 5.4 times as stable as aniline, not so stable as <i>p</i> -toluidine.  |
| $\beta$ -Naphthylamine .....                     | 0.025      | 14.9                            | { 4.3 times as stable as aniline, not so stable as <i>p</i> -toluidine.  |
| $\alpha$ -Naphthylamine-8-sulphonic acid .....   | 0.0103     | 6.1                             | { 10.6 times as stable as aniline, more stable than <i>p</i> -toluidine. |
| $\beta$ -Naphthylamine-6-sulphonic acid .....    | 0.0117     | 6.9                             | { 9.4 times as stable as aniline, more stable than <i>p</i> -toluidine.  |
| $\beta$ -Naphthylamine-7-sulphonic acid .....    | 0.0100     | 5.9                             | { 11 times as stable as aniline, more stable than <i>p</i> -toluidine.   |
| $\beta$ -Naphthylamine-6:8-disulphonic acid..... | 0.00539    | 3.2                             | { 20.3 times as stable as aniline, more stable than sulphanilic acid.    |
| $\beta$ -Naphthylamine-3:6-disulphonic acid..... | 0.00168    | 1                               | { 64.9 times as stable as aniline, more stable than sulphanilic acid.    |

The influence of the  $\text{SO}_3\text{H}$  group on the stability of the diazo-salts is very clearly shown here. One of these groups increases the stability of the diazo-salt considerably, whilst two have a still greater effect.

The last diazo-compound to be considered, namely, that from 8-amino- $\alpha$ -naphthol-3:6-disulphonic acid, is exceptionally stable, its decomposition constant (0.012) at  $80^\circ$  being 5.9 times less than the similar coefficient (0.079) for diazobenzenesulphonic acid. Now since the latter diazo-compound is 16.6 times more stable than diazobenzene chloride, it follows that the naphthalenoid diazo-derivative in question is 98 times more stable than that derived from aniline.

One of the most interesting facts brought out by the above experiments is that a diazo-salt and a naphthol or naphtholsulphonic acid can exist side by side up to a certain point without combining to form an azo-colouring matter. Assuming, as seems probable from the experiments of Goldschmidt (*loc. cit.*), that the hydrolytic dissociation of the diazo-salt is necessary before combination can take place, it would seem that, in the experiments described, the diazo-salt is not dissociated, especially in the presence of free hydrochloric acid, which has a retarding effect on the formation of an azo-compound, until its concentration becomes considerably lessened by its own gradual decomposition. When this point is reached, dissociation of the undecomposed diazo-salt takes place and the azo-colouring matter is formed.

In conclusion, we wish to thank the Farbenfabriken vorm. F. Bayer & Co., Elberfeld, and Messrs. Levinstein, Ltd., Manchester, for kindly supplying us with the amines mentioned in this paper.

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### XXIII.—*The Absorption Spectra of Metallic Nitrates.* *Part II.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

THE descriptions and measurements of spectra observed in five series of solutions of metallic nitrates examined in various ways are contained in Part I (Trans., 1902, 81, 571), accompanied by a tabular statement which shows where complete absorption occurs of all rays beyond wave-length 340 in solutions containing either gram-molecules of different nitrates or definite fractions of these proportions in a litre

of solution. The measurements were recorded in oscillation-frequencies as well as wave-lengths.\*

In the 6th series, a more intimate knowledge was sought of the bands characteristic of  $\text{NO}_3$  which are observed in solutions of the various nitrates when diluted in the proportion of one gram-molecule in 20 litres, and at intermediate stages down to 100 litres. Some notable differences were observed, particularly in the curves drawn from the spectra of salts with high molecular weights.

The coloured nitrates of cobalt and nickel were examined because they each show two absorption bands, one belonging to the metal and the other to the  $\text{NO}_3$  ion; they were compared with cupric nitrate which, under precisely similar conditions, shows no absorption band whatever.

#### *Preparation of the Nitrate Solutions.*

This series of solutions was made in such a manner that the spectra observed would all be strictly comparable with those of the nitrates of the monad metals and with ethyl nitrate. Specially prepared pure carbonates were each digested with 100 c.c. of double normal nitric acid for a period of from two to five days, after which each solution was made up to 200 c.c. with distilled water. The solutions were for the most part quite neutral, others very nearly so. After their spectra had been photographed, they were analysed with great care, the actual quantity of base in each solution being very accurately determined. The following were the figures thus obtained, expressed as grams of nitrate contained in a litre of solution:

|  | Found. | Calculated. |  | Found. | Calculated. |
|--|--------|-------------|--|--------|-------------|
| $\frac{\text{Ca}(\text{NO}_3)_2}{2}$ ..... | 20.5   | 20.0        | $\frac{\text{Zn}(\text{NO}_3)_2}{2}$ ..... | 31.2   | 32.7        |
| $\frac{\text{Sr}(\text{NO}_3)_2}{2}$ ..... | 43.3   | 43.8        | $\frac{\text{Mn}(\text{NO}_3)_2}{2}$ ...   | 26.87  | 27.5        |
| $\frac{\text{Pb}(\text{NO}_3)_2}{2}$ ..... | 102.1  | 103.4       | $\frac{\text{Ni}(\text{NO}_3)_2}{2}$ ..... | 96.83  | 95.35       |
| $\frac{\text{Cd}(\text{NO}_3)_2}{2}$ ..... | 53.7   | 56.0        |  |        |             |

When double normal nitric acid is saturated with bismuth carbonate, the addition of water would, if the compound  $\text{Bi}(\text{NO}_3)_3$  is formed, result in the solution containing  $\text{BiO}\cdot\text{NO}_3$  and free nitric acid. The

\* There is a misprint relating to sodium; " $1/\lambda$  3938" should read  $1/\lambda$  2938. The absorption spectrum due to thorium nitrate is made to appear very intense, as if  $1/100$ th of a gram-molecule in a litre absorbed all rays beyond  $1/\lambda$  2893 when 200 mm. of the solution are examined. The fraction should be  $1/4$ th of a gram-molecule, and in the case of erbium it should be  $1/6$ th of a gram-molecule.



quantity found in the bismuth nitrate solution corresponded to 28.6 grams of  $\text{BiO}\cdot\text{NO}_2$  per litre, but that calculated for  $\text{Bi}(\text{NO}_3)_3$  was 224.5 grams. This wide discrepancy shows that the substance in solution must have been the oxy-nitrate. The extraordinary absorption shown by the nitrate solution, considering the small quantity of the salt present and the wide departure from the characteristic nitric acid curve which the spectra photographed from the bismuth nitrate solution exhibit, are facts of great interest.

The large atomic mass of bismuth is a factor which may be taken into consideration, and, in this respect, the absorption spectra of the nitrate solution may be compared with those of lead and cadmium nitrates.

The solutions of cobalt, nickel, and copper nitrates, which were neutral to litmus, deposited traces of either hydroxide or carbonate which had been held in solution by the metallic nitrate. These deposits were not observed until after the solutions had been kept for some months.

The curves (p. 224) drawn from the measurements show several variations, more especially in the most characteristic part of the curves. The following are the spectrum measurements obtained from normal solutions at different dilutions from 1 in 20 to 1 in 100, the column of liquid being, in each case, 200 mm. in length.

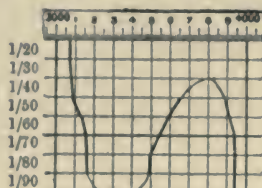
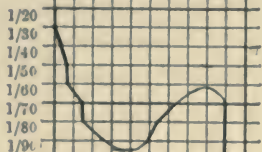
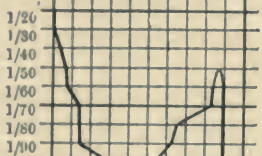
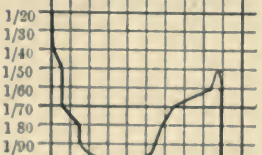
*6th Series.—Potassium Nitrate.*

Normal solution.

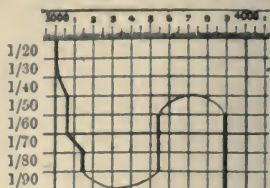
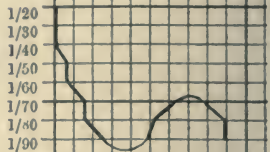
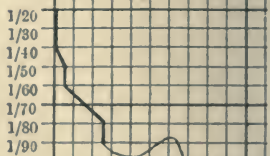
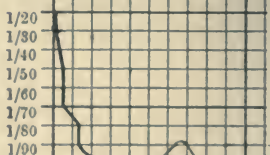
| Dilution. | Spectrum continuous<br>to |                  |                   |
|-----------|---------------------------|------------------|-------------------|
|           | $1/\lambda$ .             |                  |                   |
| 1/20      | 3002                      |                  |                   |
| 1/30      | 3002 very feebly to 3045. |                  | Rays transmitted. |
| 1/40      | 3065.                     |                  | $1/\lambda$ .     |
| 1/50      | 3065.                     | Absorption band. | A line at 3638.   |
|           |                           | $1/\lambda$ .    |                   |
| 1/60      | 3065.                     | 3149 to 3638.    | 3638 to 3889.     |
| 1/70      | 3149.                     | 3149 „ 3542.     | 3542 „ 3889.      |
| 1/80      | 3149.                     | 3323 „ 3492.     | 3492 „ 3889.      |

At the last dilution, as the band is weak, lines are seen at 3262 and 3323, but very feebly transmitted.

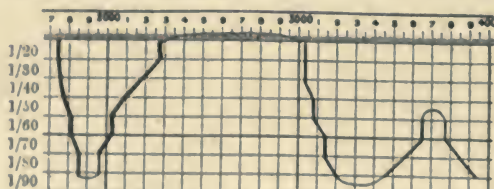
Scale of oscillation-frequencies.

 $\text{HNO}_3$   
3rd Series $\text{KNO}_3$   
 $\text{Mg}(\text{NO}_3)_2$   
6th Series $\text{Ca}(\text{NO}_3)_2$   
6th Series $\text{Sr}(\text{NO}_3)_2$   
6th Series

Scale of oscillation-frequencies.

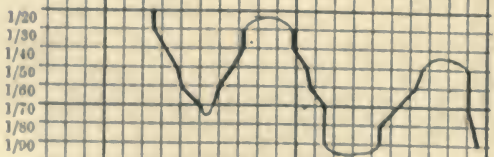
 $\text{Cd}(\text{NO}_3)_2$   
6th Series $\text{Mn}(\text{NO}_3)_2$   
6th Series $\text{BiO} \cdot \text{NO}_3$   
6th Series $\text{Pb}(\text{NO}_3)_2$   
6th Series

6th Series



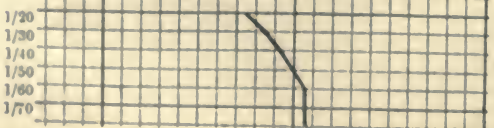
Cobalt Nitrate

6th Series



Nickel Nitrate

6th Series



Copper Nitrate

If here the curved lines are thin the transmitted spectrum is feeble.

*6th Series.—Magnesium Nitrate.*

Normal solution.

| Dilution. | Spectrum continuous<br>to |  |                             |
|-----------|---------------------------|--|-----------------------------|
|           | $\frac{1}{\lambda}$ .     |  |                             |
| 1/20      | 3010.                     |  |                             |
| 1/30      | 3010.                     |  | Rays feebly<br>transmitted. |
|           |                           | Absorption band.                         | $\frac{1}{\lambda}$ .       |
| 1/40      | 3079.                     | $\frac{1}{\lambda}$ .                    | 3668 to 3854.               |
| 1/50      | 3079.                     | 3079 to 3668.                            | 3668 „ 3915.                |
| 1/60      | 3086.                     | 3086 „ 3556.                             | 3556 „ 3915.                |
| 1/70      | 3165.                     | 3165 „ 3516.                             | 3516 „ 3915.                |
| 1/80      | 3390                      | Feeble transmission<br>of isolated rays. | 3471 „ 3915.                |

In making the above measurements, the general curve of absorption was drawn on the glass surface of the plate with red ink, so as to avoid errors by reading feeble isolated lines as if they were the termination of rays continuously transmitted.

*6th Series.—Magnesium Nitrate.*

Normal solution.

Dilution, 1/20 to 1/100. The spectra were at each stage exactly like those of potassium nitrate.

*6th Series.—Calcium Nitrate.*

Normal solution.

| Dilution. | Spectrum continuous<br>to |                       |                       |
|-----------|---------------------------|-----------------------|-----------------------|
|           | $\frac{1}{\lambda}$ .     |                       |                       |
| 1/20      | 3002.                     |                       |                       |
| 1/30      | 3045.                     |                       |                       |
| 1/40      | 3065.                     |                       | Rays transmitted.     |
|           |                           | Absorption band.      | $\frac{1}{\lambda}$ . |
| 1/50      | 3065.                     | $\frac{1}{\lambda}$ . | 3840 to 3889.         |
| 1/60      | 3065 feeble to 3149.      | 3149 to 3840.         | 3840 „ 3890.          |
| 1/70      | 3149.                     | 3149 „ 3650.          | 3650 „ 3890.          |
| 1/80      | 3149.                     | 3149 „ 3630.          | 3630 „ 3890.          |
| 1/90      | 3149 feeble to 3323.      | 3323 „ 3540.          | 3540 „ 3890.          |



*6th Series.—Strontium Nitrate.*

## Normal solution.

| Dilution. | Spectrum continuous<br>to |                       |                       |
|-----------|---------------------------|-----------------------|-----------------------|
|           | $\frac{1}{\lambda}$ .     |                       |                       |
| 1/20      | 3002.                     |                       |                       |
| 1/30      | 3002.                     | Absorption band.      | Rays transmitted.     |
| 1/40      | 3002 very feebly to 3066. | $\frac{1}{\lambda}$ . | $\frac{1}{\lambda}$ . |
| 1/50      | 3066.                     | 3066 to 3830.         | 3830 to 3889.         |
| 1/60      | 3066.                     | 3066 „ 3638.          | 3638 „ 3889.          |
|           |                           |                       | very feeble.          |
| 1/70      | 3066 very feebly to 3149. | 3149 „ 3590.          | 3590 to 3889          |
|           |                           |                       | feeble.               |
| 1/80      | 3066 very feebly to 3149. | 3149 „ 3542.          | 3542 to 3889          |
|           |                           |                       | feeble.               |

*6th Series.—Cadmium Nitrate.*

## Normal solution.

| Dilution. | Spectrum continuous<br>to |                       |                       |
|-----------|---------------------------|-----------------------|-----------------------|
|           | $\frac{1}{\lambda}$ .     |                       |                       |
| 1/20      | 3002.                     |                       |                       |
| 1/30      | 3002 very feebly to 3023. | Absorption band.      | Transmitted           |
| 1/40      | 3065.                     | $\frac{1}{\lambda}$ . | very feebly.          |
| 1/50      | 3065.                     |                       | $\frac{1}{\lambda}$ . |
| 1/60      | 3065.                     | 3065 to 3540.         | 3540 to 3889.         |
| 1/70      | 3065 feebly 3149.         | 3065 „ 3540.          | 3540 „ 3889.          |
| 1/80      | 3065 feebly 3149.         | 3149 „ 3540.          | 3540 „ 3889.          |
|           |                           | 3149 „ 3540.          | 3540 „ 3889.          |

*6th Series.—Manganese Nitrate.*

## Normal solution.

| Dilution. | Spectrum continuous<br>to |                       |                       |
|-----------|---------------------------|-----------------------|-----------------------|
|           | $\frac{1}{\lambda}$ .     |                       |                       |
| 1/20      | 3002.                     |                       |                       |
| 1/30      | 3002.                     |                       |                       |
| 1/40      | 3066.                     | Absorption band.      | Rays transmitted.     |
| 1/50      | 3066.                     | $\frac{1}{\lambda}$ . | $\frac{1}{\lambda}$ . |
| 1/60      | 3149.                     | 3149 to 3638.         | 3638 to 3770.         |
| 1/70      | 3149.                     | 3149 „ 3529.          | 3529 „ 3889.          |
| 1/80      | 3149 feebly to 3263.      | 3263 „ 2492.          | 3492 „ 3889.          |

6th Series.—*Lead Nitrate.*

Normal solution.

| Dilution. | Spectrum continuous<br>to |                  |                                  |
|-----------|---------------------------|------------------|----------------------------------|
|           | $1/\lambda$ .             |                  |                                  |
| 1/20      | 3021.                     |                  |                                  |
| 1/30      | 3021 line at 3065.        |                  |                                  |
| 1/40      | 3065 line at 3082.        |                  |                                  |
| 1/50      | 3086.                     |                  |                                  |
| 1/60      | 3093.                     | Absorption band. | Rays transmitted<br>very feebly. |
| 1/70      | 3075.                     | $1/\lambda$ .    | $1/\lambda$ .                    |
| 1/80      | 3075.                     | 3075 to 3550.    | 3550 to 3915.                    |

There is barely an indication of the absorption band in this nitrate. In this respect, the spectrum curve resembles that of bismuth.

6th Series.—*Bismuth Nitrate.*28.6 grams of  $\text{BiO}\cdot\text{NO}_3$  per litre in normal nitric acid solution.

| Dilution. | Spectrum continuous<br>to      |                  |                   |
|-----------|--------------------------------|------------------|-------------------|
|           | Isolated<br>$1/\lambda$ lines. |                  |                   |
| 1/20      | 3017. 3065.                    |                  |                   |
| 1/30      | 3017. 3082.                    |                  |                   |
| 1/40      | 3017. 3082.                    |                  |                   |
| 1/50      | 3017. 3086.                    |                  |                   |
| 1/60      | 3017. 3086—3172.               | Absorption band. | Rays transmitted. |
| 1/70      | 3017. 3086—3172.               | $1/\lambda$ .    | $1/\lambda$ .     |
| 1/80      | 3172. 3285.                    | 3285 to 3537.    | 3537 to 3674.     |

6th Series.—*Cupric Nitrate.*

Normal solution.

The spectrum of this substance is much weakened from  $1/\lambda$  2463 to 2783, and particularly about the region of the yellow rays  $1/\lambda$  1696.

| Dilution. | Spectrum continuous<br>to |                   |                               |
|-----------|---------------------------|-------------------|-------------------------------|
|           | $1/\lambda$ .             | Rays visible.     |                               |
| 1/20      | 2778.                     | 2860.             |                               |
| 1/30      | 2778.                     | 2929 very feebly. |                               |
| 1/40      | 2778.                     | 2972 feebly.      |                               |
| 1/50      | 2972.                     | 3050.             |                               |
| 1/60      | 3053.                     |                   |                               |
| 1/70      | 3053.                     | 3135 feebly.      | All rays beyond are absorbed. |
| 1/80      | 3065.                     | 3135.             |                               |

No absorption band visible in this nitrate.

*6th Series.—Cobalt Nitrate.*

Normal solution, prepared from the carbonate.

| Dilu-<br>tion. | Rays trans-<br>mitted.<br><sup>1</sup> / <sub>λ</sub> . | First<br>Absorption<br>band.<br><sup>1</sup> / <sub>λ</sub> . | Rays<br>transmitted.<br><sup>1</sup> / <sub>λ</sub> . | Second<br>Absorption<br>band. Feeble.<br><sup>1</sup> / <sub>λ</sub> . | Rays<br>transmitted.<br><sup>1</sup> / <sub>λ</sub> . |
|----------------|---|---|---|--|---|
| 1/20           | 1665 to 1719  | 1719 to 2270  | 2270 to 3006  |  |   |
| 1/30           | 1665 „ 1730   | 1730 „ 2312   | 2312 „ 3606   |  |   |
| 1/40           | 1665 „ 1742   | 1742 „ 2093   | 2093 „ 3072   |  |   |
| 1/50           | 1665 „ 1811   | 1811 „ 2030   | 2030 „ 3072   |  |   |
| 1/60           | 1665 „ 1811   | 1811 „ 2030   | 2030 „ 3165   | 3765 to 3668   | 3668 to 3780  |
| 1/70           | 1665 „ 1833   | 1833 „ 2030   | 2030 „ 3165   | 3165 „ 3507  | 3507 „ 3852   |
| 1/80           | 1665 „ 1833   | 1833 „ 1997<br>Weak.  | 1997 „ 3188<br>Rays feeble<br>to 3343.                | 3343 „ 3474  | 3472 „ 2920   |

*Nickel Nitrate.*

Normal solution, prepared from the carbonate.

| Dilu-<br>tion. | Spectrum<br>continuous<br>to<br><sup>1</sup> / <sub>λ</sub> . | First<br>Absorption<br>band.<br><sup>1</sup> / <sub>λ</sub> . | Rays<br>transmitted.<br><sup>1</sup> / <sub>λ</sub> . | Second<br>Absorption<br>band.<br><sup>1</sup> / <sub>λ</sub> . | Rays<br>transmitted<br>to<br><sup>1</sup> / <sub>λ</sub> . |
|----------------|---|---|---|--|--|
| 1/20           | 2279  | 2279 to 2759  | 2759 to 2990  |  |  |
| 1/30           | 2327  | 2327 „ 2710   | 2710 „ 2990   |  |  |
| 1/40           | 2373  | 2373 „ 2677   | 2677 „ 3065   |  |  |
| 1/50           | 2391  | 2391 „ 2619   | 2619 „ 3079   | 3079 to 3650   | 3903   |
| 1/60           | 2534  | 2534 „ 2568   | 2568 „ 3157   | 3157 „ 3538  | 3903   |
| 1/70           | 3157  |   |   | 3159 „ 3474  | 3936   |
| 1/80           | 3180  | Rays transmitted feebly to<br>3330 and again to 3474.         |   | 3180 „ 3474  | 3942   |
| 1/90           |   |   |   |  |  |

*7th Series.*—It was considered desirable to examine a number of definitely hydrated salts with high molecular weights, and those selected as being most suitable were the nitrates of thorium, erbium, and uranium. These were carefully analysed to determine the base, acid, and combined water, the last constituents being estimated by difference.\* Normal solutions were examined in thicknesses varying from 200 mm. to 2 mm., which is equivalent to a dilution of 1/100.

\* The analyses of the thorium, erbium, and uranyl nitrates were made by Mr. J. Holms Pollok, B.Sc., Assistant Chemist, Royal College of Science, Dublin, to whom my thanks are due.



7th Series.—*Thorium Nitrate*,  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$  [ $\text{Th} = 231.5$ ].

(a) Normal solution: 26.36 grams in 200 c.c. equivalent to 62 grams of  $\text{NO}_3$  per litre.

| Thickness. | Spectrum continuous to |  |                  |                   |
|------------|------------------------|--|------------------|-------------------|
| mm.        | $1/\lambda$ .          |  |                  |                   |
| 200        | From 1696 to 2787.     |  |                  |                   |
| 100        | 2877.                  |  |                  |                   |
| 50         | 2980.                  |  |                  |                   |
| 40         | 2980.                  |  |                  |                   |
| 35         | 2980.                  |  |                  |                   |
| 30         | 3002.                  |  | $1/\lambda$ .    |                   |
| 20         | 3002.                  |  | 3065.            |                   |
| 15         | 3002.                  |  | 3065.            |                   |
| 10         | 3065.                  |  |                  | Rays transmitted. |
| 5          | 3065.                  |  | Absorption band. | $1/\lambda$ .     |
| 4          | 3065. Line 3149.       |  | $1/\lambda$ .    | 3556 to 3927.     |
| 3          | 3065. „ 3149.          |  | Very feeble.     | 3556 „ 3927.      |
| 2          | 3065. „ 3149.          |  | 3354 to 3510.    | 3510 „ 3960.      |

Through 200 mm., the most extreme line photographed is  $1/\lambda$  2883 or  $\lambda$  3466.

At a thickness of 2 mm., there is a sudden extension of the spectrum, which is accounted for by the existence of a feeble absorption band between 3149 and 3537. The rays, very feebly transmitted where this band may be traced, are 3266, and three others to 3519. Beyond this point, the rays are transmitted somewhat less feebly up to 3960, at which point the spectrum ends.

(b) The normal solution diluted, 1 to 100 volumes.

| Thickness. | Spectrum continuous to |                  |                   |  |
|------------|------------------------|------------------|-------------------|--|
| mm.        | $1/\lambda$ .          | Absorption band. | Rays transmitted. |  |
| 200        | 3072.                  | $1/\lambda$ .    | $1/\lambda$ .     |  |
| 100        | 3072.                  | 3354 to 3537.    | 3537 to 3960.     |  |
| 50         | 3072.                  |                  | 3960.             |  |
| 40         | 4006.                  |                  | 3960.             |  |
| 35         | 4006.                  |                  |                   |  |
| 30         | 4006.                  |                  |                   |  |
| 20         | 4128.                  |                  |                   |  |
| 15         | 4128.                  |                  |                   |  |
| 10         | 4128.                  |                  |                   |  |
| 5          | 4176.                  |                  |                   |  |
| 4          | 4176.                  |                  |                   |  |
| 3          | 4220.                  |                  |                   |  |
| 2          | 4320.                  |                  |                   |  |

7th Series.—*Erbium Nitrate*,  $\text{Er}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$  [ $\text{Er} = 116$ ].

Normal solution: 32.64 grams in 200 c.c. equivalent to 62 grams of  $\text{NO}_3$  per litre.

| Thickness. | Spectrum transmitted continuously from $1/\lambda$ 1765 to |                  |                   |
|------------|--|------------------|-------------------|
| mm.        | $1/\lambda$ .  |                  |                   |
| 200        | 2929.  |                  |                   |
| 100        | 2961.  |                  |                   |
| 50         | 2961.  |                  |                   |
| 40         | 3005.  |                  |                   |
| 30         | 3005.  |                  |                   |
| 25         | 3021.  |                  |                   |
| 20         | 3021.  |                  |                   |
| 10         | 3085.  | Absorption band. | Rays transmitted. |
| 5          | 3085.  | $1/\lambda$ .    | $1/\lambda$ .     |
| 4          | 3172.  | 3085 to 3864.    | 3864 to 3920.     |
| 3          | 3172.  | 3172 „ 3568.     | 3568 „ 3920.      |
| 2          | 3172.  | 3172 „ 3474.     | 3474 „ 3920.      |
|            | 3295.  | 3295 „ 3363.     | 3363 „ 3940.      |

Isochromatic plates were used, and the bands characteristic of erbium, photographed by Liveing in solutions of the nitrate, were easily recognised, but being narrow, owing to the small dispersion, only the centre of each band was measured. They had approximately the following oscillation-frequencies and wave-lengths. These bands disappear when the liquid layer is reduced in thickness to about 25 mm.

| Scale numbers.<br>Hundredths of<br>an inch. | $1/\lambda$ . | $\lambda$ . | Liveing's<br>measurements.<br>$\lambda$ . |
|---|---------------|-------------|---|
| 39.0  | 1912          | 5227        | 523                                       |
| 47.5  | 2063          | 4990        | 488                                       |
| 66.5  | 2197          | 4550        | 449                                       |
| 87.0  | 2391          | 4181        | 415                                       |
| 97.5  | 2485          | 4024        | 404                                       |
| 103.5                                       | 2582          | 3870        | 387                                       |
| 114.5                                       | 2631          | 3799        | 377                                       |
| 127.0                                       | 2735          | 3656        | 365                                       |
| 143.0                                       | 2862          | 3492        | —   |

} Ultra-  
violet

7th Series.—*Uranyl Nitrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [ $\text{U} = 119.9$ ].

(a) Normal solution : 25.2 grams in 100 c.c. equivalent to 62 grams of  $\text{NO}_3$  per litre.

| Thickness. | Spectrum continuous      |                  |                   |
|------------|--------------------------|------------------|-------------------|
| mm.        | $1/\lambda$ .            |                  |                   |
| 200        | from 1695 to 1901.       |                  |                   |
| 100        | 1665 „ 1956.             |                  |                   |
| 50         | 1665 „ 2040.             |                  |                   |
| 40         | 2040.                    |                  |                   |
| 30         | 2040.                    |                  |                   |
| 25         | 2040.                    |                  |                   |
| 20         | 2040.                    |                  | Rays transmitted. |
| 15         | 2113.                    | Absorption band. | very feebly.      |
| 10         | $1/\lambda$ .            |                  | $1/\lambda$ .     |
| 5          | 2133.                    | 2133 to 2661     | 2611 to 2759      |
| 4          | 2173.                    | 2173 „ 2609      | 2609 „ 2759       |
| 3          | 2250.                    | 2250 „ 2595      | 2595 „ 2797       |
| 2          | 2326.                    | 2326 „ 2445      | 2445 „ 2797       |
|            | Rays continuous to 2797. |                  |                   |

No other bands were distinctly photographed, but there was a weakening of the spectrum at points below  $1/\lambda$  2040 ( $\lambda$  4686).

(b) A second solution, made by diluting to 1/100th the normal strength.

| Thickness. | Rays continuous to |                             |
|------------|--------------------|-----------------------------|
| mm.        | $1/\lambda$ .      |                             |
| 200        | 2797.              |                             |
| 100        | 2991.              |                             |
| 50         | 3079.              | Isolated lines very feeble. |
| 40         | 3079.              | $1/\lambda$ .               |
| 30         | 3079.              | 3157                        |
| 25         | 3079.              | 3157, 3310.                 |
| 20         | 3157.              | 3279, 3330.                 |
| 15         | 3343.              | 3537, 3662.                 |
| 10         | 3343.              | 3537, 3662.                 |
| 5          | 3537.              | 3780.                       |
| 4          | 3537.              | 3903.                       |
| 3          | 3537.              | 3903.                       |
| 2          | 3662.              | 3903.                       |

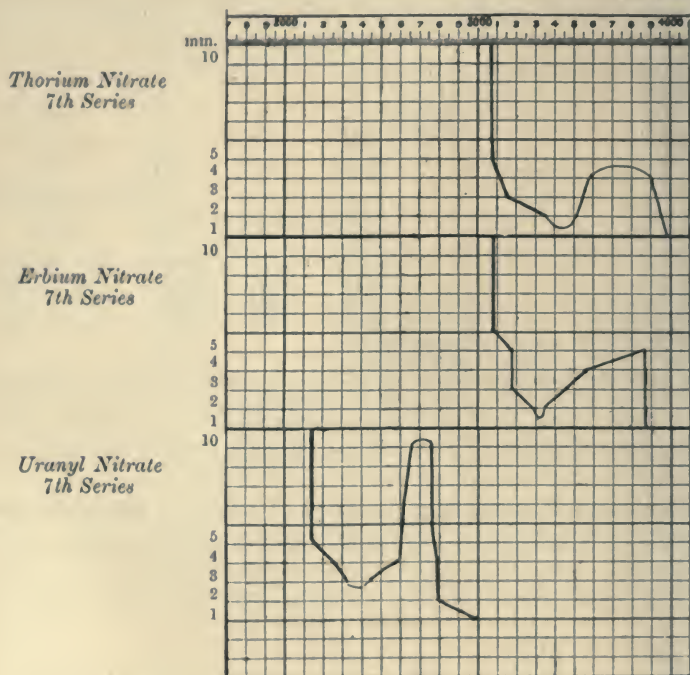
The beautiful photographs of the erbium nitrate spectra under varying conditions, published by Liveing, cannot be surpassed, but unfortunately they do not extend beyond  $1/\lambda$  2905, at which point the  $\text{NO}_3$  band only commences (*Trans. Camb. Phil. Soc.*, 1900, 18, 298).

It was thought that thorium salts might show the existence of a band or bands due to the metal, but on converting the nitrate into



chloride by repeatedly evaporating it to dryness with strong hydrochloric acid it was found that this was not the case, the absorption being quite continuous at all dilutions.

*Scale of oscillation-frequencies.*



*Where the curved lines are thin it indicates that the spectrum is feebly transmitted.*

The thorium, erbium, and uranyl nitrates exhibit wide differences. The first two differ, but the  $\text{NO}_3$  band is not widely displaced, and therefore it might be considered as probable that with thorium nitrate, a salt which in solution deposits a basic compound after the lapse of three or four months, the dissociation is not of the same kind but hydrolytic. There is, however, no proof of this. The uranyl nitrate exhibits the  $\text{NO}_3$  band in quite a different position, and here it is evident, either that the salt is not dissociated at all, or that it is dissociated into complex ions, in one of which the  $\text{NO}_3$  group is associated with uranium, and in consequence its rate of vibration is greatly retarded, as might be expected from the greater atomic mass of the uranium. Lastly, it may be remarked that cobalt and nickel nitrates each exhibit two bands, one belonging to the cation, and one to the anion.

The cation in each case shows a band in the chloride, bromide, and iodide, which has a different character in each halogen salt. Their measurements are, however, not recorded in the present communication.

*The Absorption Spectra of Ethyl Nitrate and Nitric Acid.*

It was necessary, in order to complete these observations, to examine, independently of Soret and Rilliet's results, the spectrum of ethyl nitrate as photographed through different thicknesses of the pure compound and also through alcoholic solutions of graduated dilution. Nitric acid, both strong and dilute, was also examined.

The ethyl nitrate was very carefully prepared, and nearly the whole of the liquid boiled at  $87^{\circ}$  under 30.0 inches pressure. It was kept in the dark until submitted to spectroscopic examination. After moistening a quantity of about 10 c.c. with water and shaking with test papers, it was found to be perfectly neutral.

*Nitric Acid, Strong and Dilute, Compared with Potassium and Sodium Nitrates.*

Very pure nitric acid of sp. gr. 1.431 was examined in a cell having a thickness of 2 mm. and afterwards placed in a cell 100 mm. thick and filled up with water. The very curious fact was noticed that the dilute solution was more strongly absorbent of the ultra-violet rays than the strong acid. This experiment has been modified in various ways and with acids of different specific gravities, but the result has been the same. It is evident that, when diluted with water, the acid undergoes some molecular changes, which will be dealt with in a further communication.

*8th Series.—Ethyl Nitrate.*

(a) Undiluted.

| Thickness.<br>mm. | Spectrum continuous<br>to<br>$1/\lambda$ . | Lines transmitted.       |
|-------------------|--|--------------------------|
|                   |  | $1/\lambda$ .            |
| 10                | 3065.                                      | 3100.                    |
| 5                 | 3114.                                      | 3132 very faint.         |
| 4                 | 3157.                                      |                          |
| 3                 | 3157.                                      |                          |
| 2                 | 3157.                                      | Undefined to about 3193. |

(b) An *N*/10 alcoholic solution (0.91 gram in 100 grams of alcohol, b. p. 78°).

| Thickness. | Spectrum continuous<br>to |                                     |
|------------|---------------------------|-------------------------------------|
| mm.        | $1/\lambda$ .             | Lines transmitted.<br>$1/\lambda$ . |
| 200        | 3157.                     |                                     |
| 100        | 3193.                     | 3169 and 3300.                      |
| 50         | 3399.                     | 3487 very faint.                    |
| 40         | 3399.                     | 3487, 3577.                         |
| 35         | 3399.                     | 3487, 3577.                         |
| 30         | 3399.                     | 3487, 3577.                         |
| 20         | 3587.                     | 3656, 3840.                         |
| 15         | 3587.                     | 3656, 3901.                         |
| 10         | 3587.                     | 3656, 3915.                         |
| 5          | 3895.                     | 3901, 3917.                         |
| 4          | 4061.                     | 4090 faint.                         |
| 3          | 4061.                     | 4090 faint and 4184.                |
| 2          | 4061.                     | 4128 faint and 4184.                |

There is no indication of an absorption band. The isolated lines, which are more or less weakly transmitted, simply indicate that the transmission of the rays does not terminate abruptly.

It was found desirable to submit pure anhydrous lithium nitrate dissolved in anhydrous alcohol (b. p. 78°) to the same method of examination as that performed on ethyl nitrate in order to make a strict comparison between the behaviour of an organic and an inorganic salt. The results show a marked difference between the constitution of the ethyl nitrate and that of the solution of the metallic salt. Whereas the ethyl nitrate gave no indication of the existence of the  $\text{NO}_3$  group in the molecule under any conditions, the lithium nitrate, on the other hand, in the perfectly anhydrous alcoholic solution, showed distinctly the absorption band characteristic of a nitrate, as if, in fact, the salt molecule consisted of two parts, Li and  $\text{NO}_3$ .





*8th Series.—Sodium Nitrate.*

## Normal solution.

| Thickness. | Spectrum continuous to |  |               |
|------------|------------------------|--|---------------|
| mm.        | $1/\lambda$ .          |  | $1/\lambda$ . |
| { 10       | 3045.                  | Isolated line very feebly transmitted .....  | 3825          |
|            | 100                    | 3045. Isolated strong lines feebly transmitted, 3638, 3695, 3825, 3886.  |               |
| { 5        | 3045.                  | Isolated strong lines feebly transmitted, 3638, 3695, 3761, 3825, and 3886.  |               |
|            | 100                    | 3045. Strong line very feebly transmitted .....<br>Isolated strong lines feebly transmitted, 3638, 3695, 3761, 3825, and 3886.<br>Both spectra equally strong. | 3135          |
| { 4        | 3065.                  | Isolated strong line feebly transmitted .....<br>Very feeble, 3521, 3638, 3695, 3761, 3782, 3804, 3825, 3854, and 3889.  | 3135          |
|            | 100                    | 3065. Line about .....<br>Very feeble, 3521, 3568, 3638, 3695, 3761, 3782, 3825, and 3889.<br>The two spectra are quite alike.                                 | 3135          |
| { 2        | 3065.                  | Very feeble continuous rays.....   | 3106          |
|            |                        | Strong line, 3065. Strong line appearing feeble, 3264. Lines appear but weakly to 3927.  |               |
| { 100      | 3065.                  | Absolutely the same to.....<br>The absorption band has almost disappeared.   | 3927          |

*8th Series.—Potassium Nitrate.*

## Normal solution.

| Thickness. | Spectrum continuous to |  |  |
|------------|------------------------|--|--|
| mm.        | $1/\lambda$ .          |  |  |
| { 10       | 3045.                  | Isolated line 3825.  |  |
|            | 100                    | 3045. Isolated strong lines appearing feeble, 3638, 3695, 3761, 3825, and 3889.                        |  |
| { 5        | 3045.                  | Isolated strong lines very feebly transmitted, about 3135, 3638, 3695, 3761, 3825, and 3889.           |  |
|            | 100                    | 3045. Exactly similar.   |  |
| { 4        | 3065.                  | A line about 3135 very feebly transmitted, 3500, 3521, 3568, 3598, 3638, 3695, 3761, 3782, 3804, 3825. |  |
|            | 100                    | 3065. Exactly similar, though, if any difference, possibly a little stronger.                          |  |
| { 2        | 3135.                  | Rays transmitted, 3184, 3264, 3296, 3323, 3355, 3453, 3492, 3529, and 3927.                            |  |
|            | 100                    | 3135. Exactly similar.   |  |

*The Absorption Spectra of Sulphuric and Hydrochloric Acids in Normal Solutions.*

A normal solution of sulphuric acid transmits, through a column of liquid 200 mm. in length, a spectrum which is continuous to  $1/\lambda$  4413 and but slightly enfeebled from this point to  $1/\lambda$  4555. The same solution through 100 mm. transmits a spectrum which is practically that of water. In the same way, a normal solution of hydrochloric acid transmits a spectrum which, through 200 mm., does not differ essentially from the spectrum of water up to  $1/\lambda$  4555, there being only a slight enfeeblement of the rays from  $1/\lambda$  4460. A thickness of 100 mm. transmits the rays as freely as a similar column of water.

*The Effect of Light on Certain of the Solutions.*—It has been mentioned that some of the haloid salts of nickel and cobalt, especially in concentrated solutions, are decomposed when protected from access of air but exposed to ordinary daylight, the action taking place where the light is absorbed by the solution. The following notes were made of the changes observed in solutions of the nitrates when they had been put aside after the examination of their spectra. The solutions of nitrates of normal strength had been preserved for two years in colourless, cylindrically-shaped, well-stoppered bottles nearly filled with liquid and standing in a glass case, but not exposed to sunshine.

$\frac{\text{Cu}(\text{NO}_3)_2}{2}$ .—Very slight light brown deposit. No iron present.

$\frac{\text{Ni}(\text{NO}_3)_2}{2}$ .—A pale green precipitate which rendered the liquid decidedly turbid.

$\frac{\text{Co}(\text{NO}_3)_2}{2}$ .—A red solution with a rather copious brown precipitate which adhered to the glass like a skin.

$\frac{\text{Mn}(\text{NO}_3)_2}{2}$ .—A brown precipitate, more copious where there were drops of liquid on the glass or where a thin layer of the liquid adhered to the glass.

Bismuth nitrate.—A slight, but dense, granular precipitate was deposited.

$\frac{\text{Th}(\text{NO}_3)_4}{4}$ .—A dense, white precipitate which, after shaking rapidly, settled. Thorium chloride behaved in a precisely similar manner.

$\frac{\text{Pb}(\text{NO}_3)_2}{2}$ .—Deposited a very slight, but dense, white precipitate.

Uranyl nitrate remained perfectly clear. A pure neutral solution



of manganese sulphate has a pale pink colour; after a few days, it becomes colourless, it next changes to pale yellow, then to a clear brown liquid, which finally becomes turbid.

### *Discussion of the Results.*

The results obtained in the course of various investigations of the absorption spectra of solid salts and saline solutions must be taken into account in any attempt to elucidate the constitution of the latter.

Bunsen (*Pogg. Ann.*, 1866, 128, 100) examined didymium salts in the crystalline state as well as in solution and found that the width of the absorption bands varied with the thickness of the absorbing medium and with the quantity of salt contained in it. Solutions of the chloride, sulphate, and acetate, each containing the same weight of didymium, yielded different spectra, the bands being shifted towards the red end of the spectrum with increase in the molecular weight of the salt.

Not only one or two, but each of the bands near the Fraunhofer lines, D, E, and F, suffered displacement.

H. Becquerel has more recently observed such variations (*Compt. rend.*, 1887, 104, 777, and 1691) both in crystals and in solutions of the salts. His measurements were made with an instrument of smaller dispersion than that employed by Bunsen, and hence the differences in the spectra of solutions of different salts do not appear so remarkable. Muthmann and Stützel, "Beiträge zur Spectral-analyse von Neodym und Praseodym" (*Ber.*, 1899, 32, 2653), recognised great differences between the spectra of solutions of the nitrate, chloride, and carbonate of neodymium. The last compound differs from the other two by possessing a somewhat intense blue colour. The intensity of the absorption was greatly increased; the band in the violet,  $\lambda$  432—434, was no longer visible, and that in the green was stronger than in the nitrate. There was a marked alteration in the wave-lengths of the absorbed rays, which showed a shifting of the bands towards the red end of the spectrum, the maximum of absorption being altered to the extent of from 7 to 5 millionths of a millimetre in wave-length in the yellow and green rays. The neodymium carbonate showed, in addition, a fine, well-marked dark line in the orange at  $\lambda$  600·5, which disappeared when the carbonate was converted into salts with mineral acids. A corresponding band of less intensity was visible in the acetate at  $\lambda$  597·0. The relative intensities of the bands in the praseodymium carbonate, and also the order in which the lines disappear upon dilution, are quite different from those of the nitrate and the chloride. For instance, whilst in the nitrate solution the line of absorption in the blue is the most

persistent, in the carbonate solution that in the yellow, approximately  $\lambda$  596.5, is the last to disappear.

The authors, assuming that these changes in the spectra are due to the electrolytic dissociation of the salts by dilution, are unable to reconcile with this the fact of the neodymium exhibiting different absorption spectra when the chloride, nitrate, acetate, and carbonate are examined. On the assumption that the salts are completely resolved into ions, the neodymium ions in the solution of each salt should exhibit the several bands unchanged in position, breadth, and intensity, the neodymium being in strictly atomic proportions in each solution. The bands should furthermore weaken to the same extent and disappear in the same order upon further dilution.

Liveing has shown that concentrated solutions of the chlorides and nitrates of didymium and erbium containing equivalent quantities of metal show the same absorption spectra for each element in solutions of different concentrations.

Didymium acetate shows a modified series of bands, which are shifted more towards the red end than those of the nitrate. The tartrate in ammoniacal solution has all its bands more diffuse than the chloride, some being almost diffused away, and all the bands are shifted towards the red. The strong solutions of the nitrates, however, have a general absorption of the more refrangible rays, and in this respect they differ from those of the chloride and acetate of didymium and from that of the chloride of erbium (*Trans. Camb. Phil. Soc.*, 1900, 18, 298).

The reason of this peculiarity of the nitrates has already been explained in Part I of this communication.

Ionisation is supposed to increase with dilution, and the absorption of rays by the ions should increase in intensity by dilution when the total quantity of salts, dissociated and undissociated, through which the rays are transmitted remains the same, but the experiments on dilution recorded by Liveing militate against this view, as he has pointed out. Ionisation is an effect which should be increased by heating and diminished by acidification, but it was proved by Liveing that the effect of heating and of acidifying salts of didymium and erbium did not cause that change in their spectra which might have been anticipated. In fact, the evidence adduced by him goes very far towards precluding the possibility of the bands characteristic of these salts being produced by the metallic ions.

The effect of heat (*Sci. Trans. Roy. Dubl. Soc.*, 1900, 7, [ii], 253) on dilute and on concentrated solutions of didymium salts, and on solutions of praseodymium and neodymium ammonium nitrates, is to broaden the absorption bands without any diminution of intensity; in fact, the spectra are altered just as if a more concentrated solution of the salt were being examined. The broadening effect was on the side



of the absorption bands nearer the red. Furthermore, in the case of neodymium ammonium nitrate, there was an increased general absorption of the more refrangible rays, in fact, a considerable shortening of the spectrum, but no similar effect was seen in the corresponding praseodymium solution.

In a recently published paper (*Sci. Trans. Roy. Dubl. Soc.*, 1901, 7, [ii], 313—320), I have pointed out that certain haloid salts of copper, nickel, and cobalt, which are hygroscopic, form definite liquid hydrates when exposed to the air, and that the hydrates varied in composition with slight alterations in temperature. The observations were carried on during several months, and deductions were drawn as to the nature of these hydrates and the cause of their formation.

Carlo Rossi (*Gazzetta*, 1901, 31, ii, 502—510. Abstr., 1902, 82, 198), has made a comparison of the solubility coefficients of analogous salts expressed in the number of grams of a compound contained in 100 grams of water. Analogous salts are those with one common ion, whilst the other ions are analogous in the sense of the periodic law. From the tabulated results of observations on sixteen salts, it can be calculated that the number of water-molecules required to dissolve one molecule of salt are for barium 32, strontium 16, and calcium 8. Conversely, the numbers of molecules of the salts which saturate the same quantity of water stand in the relation therefore of 1:2:4 for the elements in the above order. It is also shown that the molecular volumes of saturated solutions of salts of analogous series have the same values at a definite temperature. This author regards such saturated solutions as representing at any definite temperature true chemical compounds, which are liquid and readily dissociated, being destroyed by the very slightest change in temperature. A similar conclusion was inevitable in the case of deliquescent salts.

The evidence that molecules of hydrated salts exist in solutions consists of a large number of well ascertained facts, but the simplest mode of expressing the character of the spectroscopic evidence is as follows. Salts of whatever nature which crystallise in the anhydrous state and do not form hydrates exhibit absorption spectra in saturated solutions made at 16° or 20°, which undergo but little change upon heating to 100°, and the nature of the change is such that it may generally be predicted for each salt. But the saturated solutions of crystalline hydrated salts undergo remarkable changes when heated, and the actual nature of such changes in their absorption spectra cannot be predicted, but they correspond either with the formation of different known hydrates or with the colour of the anhydrous salt. The sole exceptions observed among coloured compounds are certain salts of chromium, in which the nature of the change was explained,



and accounted for in the original communication (*Sci. Trans. Roy. Dubl. Soc.*, 1900, 7, [ii], 253). Dietz, Frank, von Wrochum, and Mylius have shown, from a study of the solubilities of various salts, that there are no fewer than five modifications of calcium chromate which all exist in solution within a certain range of temperature, so that at  $18^{\circ}$  as many as five distinct saturated solutions of calcium chromate may be obtained (*Wiss. Abhandl. Phys.-Tech. Reichsanstalt*, 1900, 3, 425—477; also *Abstr.*, 1897, 72, ii, 316, 442; 1899, 76, ii, 209, 221). Adie (*Trans.*, 1891, 59, 344) examined potassium nitrate at dilutions  $1/5$  (nearly),  $1/7.5$ ,  $1/10$ ,  $1/20$ ,  $1/40$ , and  $1/80$  normal, and found that by comparing the observed osmotic pressures in terms of atmospheres  $P$  with the number of times this is greater than  $\pi$  ( $\pi$  being calculated on the assumption that the ultimate osmotic pressure is the same as would be exerted by the compression of a gram-molecule of hydrogen into the same space as the solution occupies), a curve is formed which may be divided into four parts. Starting with a saturated solution, dilution diminishes the osmotic pressure until we get to  $1/7.5$ ; from there to about  $1/10$ , the pressure is almost normal, at the former point a little less, and at the latter a little more, than normal. This may represent the duration of existence of some complex molecule of the salt or of a definite hydrate.

When the dilution is  $1/10$  normal, the dissociating action of the solvent may be supposed to begin to take effect on the complex molecule of the salt. This goes on increasing through dilutions  $1/20$ ,  $1/40$ , and  $1/80$ , but does not pass beyond the line of complete dissociation into ions, which apparently coincides with this last dilution (*ibid.*, p. 352). It is precisely at these points, namely,  $1/20$ ,  $1/40$ , and down to  $1/80$  normal, that the absorption spectra show the effect of the  $\text{NO}_3$  group on the curves of the various nitrate solutions. Judging from the osmotic pressures, sodium nitrate behaves anomalously, for with a dilution of  $1/10$  normal it is in a condition between a wholly and a half dissociated salt, but at  $1/40$  it behaves as if entirely undissociated.

In connection with these osmotic pressures, Adie remarks that "as the curves are so nearly continuous, we cannot infer the existence of definite hydrates in the solutions of the salts examined. For this purpose, one must get a larger range of observations, which can be procured by some less lengthy method, such as the lowering of the freezing point."

Six other metallic nitrates were examined at dilutions of  $1/20$  and  $1/40$  of a gram-molecule per litre in order to ascertain the influence of the base upon osmotic pressures and dissociation constants. It may be remarked that at  $1/20$  the osmotic pressures of magnesium,

barium, cobalt, and copper are much greater than those of calcium and strontium, which correspond closely with those of potassium and sodium, but there are differences at 1/40 dilution.

Whatever the cause of this may be it is remarkable that the spectrum curves below 1/40 of the normal solutions of calcium and strontium nitrates differ from those of barium, but closely resemble those of sodium and potassium nitrates.

In some instances, dissociation takes place into free acid and a basic salt. Adie concludes that the action of the solvent is two-fold, and may be expressed as:

(i) "Combination of the molecules of the dissolved substance with the solvent to form complex molecules.

(ii) Separation of the complex molecules of the dissolved substance, under the action of the solvent, into simpler molecules, not necessarily as small as the limiting gaseous molecule."

The observations made independently by very different methods on the same salts, in solutions of similar strengths, lead to nearly the same conclusions as regards their molecular condition.

#### *Organic Substances of a Basic Character.*

It has already been pointed out that ethyl nitrate, whether alone or in solution, yields the same spectrum, and there is no evidence whatever that the molecule contains, or is composed of, dissimilar parts. In this respect, the esters of nitric acid are entirely different from solutions of inorganic nitrates. If we turn now to the absorption curves of nitrogenous organic bases and their hydrochlorides, the differences in the mode of vibration of the base, the acid, and the salt are in some instances very striking (Trans., 1885, 47, 685).

The substances examined were:

- (1) Pyridine and pyridine hydrochloride.
- (2) Quinoline and quinoline hydrochloride.
- (3) Tetrahydroquinoline and tetrahydroquinoline hydrochloride.
- (4) *o*-Toluidine and its hydrochloride.
- (5) *p*-Toluidine and its hydrochloride.

The differences between the spectra transmitted by the base and the salt respectively in (1) are but slight. There is a marked difference between the base and the salt in (2), and there are still greater differences in (3), (4), and (5). These differences, which are somewhat diverse in character, could in no case have been predicted, though a similarity is to be remarked between the differences noticed between base and salt in (3), (4), and (5), which the curves illustrating the original paper clearly exhibit. As the substances (1) and (2) are feebly basic, and the salts therefore easily hydrolysed, the absorption



curves of the bases differ but slightly from those of the salts. The absorption curves of the salts of the stronger bases, (3), (4), and (5), differ widely from those of the bases alone. It is to be inferred from this that they are neither completely ionised nor hydrolysed.

The conclusions arrived at and recorded at the time may here be quoted (*loc. cit.*, p. 693).

"Molecules of compounds, that is to say, molecules composed of dissimilar atoms, vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no visible relation to the chemical constituents of the molecule, whether these be atoms or smaller molecules. Hence it appears that a molecule is a distinct and individual particle which cannot be represented by our usual chemical formulæ, since these symbolise certain chemical reactions and fail to express any relation between physical and chemical properties."

This is true in the case of carbon compounds where substitution has taken place, and it also holds good for various esters and salts of organic bases, but the statement requires some modification when we deal with either alcoholic or aqueous solutions of metallic salts; for it is an incontestable fact that the  $\text{NO}_3$  group exhibits its presence in various ways when the nitrates are suitably diluted beyond 1 gram-molecule of substance in 20 litres of water, and yet we cannot affirm that the  $\text{NO}_3$  is a free and independent mobile particle under these conditions, because the influence of the base, or of the positive ion, is apparent. This fact is rendered evident as well by Adie's investigations as by the absorption spectra.

There is a remarkable difference between the constitution of ethyl nitrate, on the one hand, whether undiluted or in dilute alcoholic solution, and, on the other hand, that of the equally dilute solutions of inorganic nitrates of various kinds. The  $\text{C}_2\text{H}_5\text{NO}_3$  molecule vibrates as a whole, and there is nothing in its spectrum to indicate the existence within the molecule of any parts which can be differentiated. The nature of the differences in the absorption spectra of the inorganic nitrates, in dilutions ranging from  $\text{NO}_3$  in 20 litres of solution to  $\text{NO}_3$  in 100 litres, is that which may be expressed by saying that in nearly all cases the intramolecular vibrations characteristic of the  $\text{NO}_3$  group are clearly exhibited. With dilutions ranging from a normal solution to dilutions of 1/18 and to 1/19 normal, the nature of the absorption is generally that due to molecular vibrations only; that is to say, it is a general absorption due to the motion of the molecules, and the parts of the molecules are not differentiated. Such motion of translation is accelerated by heat, and, consequently, by raising the temperature of the solution the absorption spectrum is intensified, the effect being to give it the appearance of a stronger solution at a lower



temperature, but the spectrum is not otherwise altered. This fact is capable of a simple explanation by the action of heat causing so many more molecules to pass into the path of the rays that the effect is the same as if the solution were more concentrated.

Though evidence of what may be regarded as ionic dissociation is afforded by the absorption spectra of dilute solutions of inorganic nitrates, yet the spectra are not all alike as they would be if there was a complete resolution into  $\text{NO}_3$  and metallic ions, and in some instances the evidence is as equally favourable to the view that certain salts are resolved into  $\text{HNO}_3$  and a base. The difference between the absorption curves of various nitrates is greatest with nitrates containing cations of greatest atomic mass relatively to the  $\text{NO}_3$  ions.

An explanation applicable to all the hitherto observed facts in relation to absorption spectra and the chemical constitution of saline solutions is as follows.

Assuming the salts to be completely ionised at greater dilutions than 1/20 normal, there must still be an attraction of the positive for the negative ion which leads them to move in pairs or groups of a more or less complex character. For instance, in the case of a nitrate represented by  $\text{MNO}_3$ , where M is the metal, the rate of motion of the M may be accelerated or retarded by the  $\text{NO}_3$ , or *vice versa*, the rates of vibration being determined by the relative masses of the ions. When the mass of the positive ion is  $\text{H}=1$ ,  $\text{K}=39.15$ ,  $\text{Ag}=107.93$ ,  $\text{Tl}=204.1$ , and so on, we have  $\text{NO}_3=62$ ; but for  $\text{Cd}=112$  we have  $(\text{NO}_3)_2$ , for  $\text{Th}=232$ ,  $(\text{NO}_3)_4$ , and for  $\text{Pb}=206.9$ ,  $(\text{NO}_3)_2$ . With bismuth, the result is in all probability  $\text{BiO}\cdot\text{NO}_3$ , and therefore we have  $\text{BiO}=224$  with  $\text{NO}_3=62$ . The more powerful absorptions in regions of longer wave-lengths which characterise the salts with high molecular weights are thus accounted for. Furthermore, in dealing with magnesium, zinc, calcium, strontium, and barium nitrates, the comparatively slight differences in the absorption curves may be readily understood, while the general similarity in their spectra to the absorption band of the  $\text{NO}_3$  ion is owing to the differences in the atomic masses of the metallic ions being too small to have any appreciable effect on the absorption spectra; such, at any rate, as could be measured with instruments of small dispersion. But, as already indicated, it is otherwise in the case of elements the atoms of which are of large mass.

It has been explained that as the intramolecular vibrations are dependent on, and are a consequence of the molecular vibrations in, such compounds as benzene, triphenylmethane, naphthalene, anthracene, &c., and that where the oscillation frequencies of the molecular vibrations are retarded by the increased mass of the molecule, so

in like manner are the oscillation-frequencies of the intramolecular vibrations retarded. Accordingly we have the positive ion, in its attraction for the negative ion, causing acceleration in the rate of vibration of the negative ion when the mass of the atom is smaller than that of the  $\text{NO}_3$ , as, for instance, in the case of sodium, potassium, or lithium. Conversely, the  $\text{NO}_3$  accelerates the motion of the positive ion when the atomic mass of the latter is greater than that of the  $\text{NO}_3$ , but when the atomic mass of the positive ion is sufficiently large the difference is quite appreciable.

Attention has already been directed in Part I, p. 573, to the probable relation of electrolytic dissociation to photographic action in the following words: "there is reason to believe that the action of radiant energy or dilute solutions is of more frequent occurrence than is usually admitted or taken into account," and instances were mentioned. Since then, three remarkable communications by J. Chunder Bose have been published (*Proc. Roy. Soc.*, 1902, 70, 154—193). It is supposed on good grounds "that the effect of radiation is to produce a state of molecular strain." Experimental evidence is adduced which shows that the molecular strain caused by the action of light changes the physico-chemical properties of substances so that it becomes possible to develop a latent image through differences in chemical stability as, for instance, by reducing agents.

It is evident from their spectra that solutions of metallic nitrates, in dilutions corresponding to one gram-molecule of nitric acid in 20 to 100 litres of water, are in a condition of molecular strain, inasmuch as we possess evidence of their internal molecular vibrations in parts which have not been actually separated.

### *Conclusion.*

The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts—the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis or by static electricity and, in some instances, by photographic action.

In the case of esters such as ethyl nitrate, the conditions are seen to be entirely different because the molecule is manifestly neither dissociated nor in a state of molecular tension, there being no evidence of  $\text{NO}_3$  having entered into the composition of the compound, even



when the substance has been dissolved and diluted until the ethyl nitrate no longer causes absorption of any of the rays of the spectrum which the solvent is capable of transmitting.

## XXIV.—*Phenocycloheptene*.

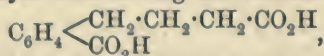
By FREDERIC STANLEY KIPPING and ALBERT E. HUNTER.

TAKING the conversion of hydrindamine hydrochloride, on heating, into the hydrocarbon indene and ammonium chloride (Kipping and Hall, *Trans.*, 1900, 77, 467) as an example of the ease with which aromatic cyclic hydrocarbons containing a partially reduced closed chain may be obtained from the corresponding saturated cyclic amines, it seemed highly probable that homologues of indene could be synthesised in a similar manner.

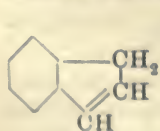
Moreover, as no hydrocarbon containing a benzene nucleus condensed with a seven-carbon ring, either reduced or partially reduced, has hitherto been prepared, the production of such a compound seemed to present an inviting subject for investigation, the results of which are here recorded.

When the dry hydrochloride of pheno- $\alpha$ -aminocycloheptane (Kipping and Hunter, *Trans.*, 1901, 79, 602) is heated at about  $240^{\circ}$ , it breaks up into ammonium chloride and an unsaturated hydrocarbon, a homologue of indene; the following equation,  $C_{11}H_{13}NH_2 \cdot HCl = C_{11}H_{12} + NH_4Cl$ , expresses this change.

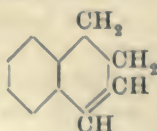
The unsaturated character of this hydrocarbon is established beyond a doubt by the ease with which it combines with bromine and by the readiness with which it is oxidised at the ordinary temperature by a dilute neutral solution of potassium permanganate; the position of the double binding is also established by the fact that the oxidation product is a dicarboxylic acid having the constitution



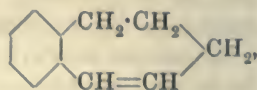
identical with the acid described by Roser (*Ber.*, 1885, 18, 3118). There is, therefore, little doubt that the hydrocarbon is a cyclic homologue of indene and of dihydronaphthalene, the series being indicated by the following formulæ:



Indene  
(Phenocyclopentene).



Dihydronaphthalene  
(Phenocyclohexene).



Phenocycloheptene.



and, in accordance with this view, we have named it *phenocycloheptene*.

This hydrocarbon displays a marked contrast to indene in its behaviour towards picric acid and towards benzaldehyde, for whereas indene readily forms with picric acid an additive compound which may be used for the identification of the hydrocarbon, *phenocycloheptene* does not give a like product; moreover, indene readily condenses with benzaldehyde in presence of a little sodium ethoxide, forming a well-defined compound, but *phenocycloheptene* cannot be made to undergo a similar condensation.

This difference in behaviour seems at first sight remarkable, considering the analogy between the constitution of indene and that of *phenocycloheptene*, but the explanation no doubt depends on the fact that the accumulation of methylene groups increases the aliphatic character of the compound. The non-formation of a picrate is thus accounted for, because, although a great many hydrocarbons containing a methenyl ( $\text{CH}_2$ ) group afford picrates, others, such as the di- and tetra-hydrobenzenes, which contain methylene groups, do not appear to form such derivatives.

A similar difference in character has also been observed in the case of the two ketones,  $\alpha$ -hydrindone and pheno- $\alpha$ -ketoheptamethylene, which correspond with the two hydrocarbons, indene and *phenocycloheptene* respectively; the former ketone is a solid melting at  $44^\circ$ , the latter is a liquid at the ordinary temperature; moreover, the oxime of  $\alpha$ -hydrindone melts at  $146^\circ$  and the phenylhydrazone at  $120^\circ$ ; the oxime of pheno- $\alpha$ -ketoheptamethylene melts at  $108$ – $109^\circ$ , whilst the phenylhydrazone, which does not crystallise at all well, decomposes with great rapidity. These differences indicate that the aliphatic character is more pronounced in the case of pheno- $\alpha$ -ketoheptamethylene than in that of  $\alpha$ -hydrindone.

#### EXPERIMENTAL.

##### *Distillation of Pheno- $\alpha$ -aminocycloheptane Hydrochloride.*

When the pure dry hydrochloride, in quantities of about 5 grams, is carefully heated in a small Würtz flask, no change is observed until a temperature of about  $240^\circ$  is reached; the mass then partly liquefies; on heating more strongly, decomposition takes place, and a neutral oil distils over together with a little solid matter, leaving behind a white substance which sublimes on the cooler parts of the flask. The oil is dissolved in ether, the solution washed with water and dried with fused calcium chloride; the ether is then distilled off and the residue fractionated. In the first distillation, practically the whole of the liquid passes over between  $231^\circ$  and  $234^\circ$ , leaving a very small quantity

of residue; the portion boiling at 231—234°, when redistilled, yields a pure product having a boiling point of 233·5—234° (757 mm. pressure), the mercury thread being entirely immersed in the vapour.

In order to prove that the decomposition proceeds as in the case of hydrindamine hydrochloride, the sublimate was examined and was found to be ammonium chloride.

*Phenocycloheptene*, thus obtained, is a colourless, mobile, highly refractive liquid having a rather strong odour, recalling that of naphthalene or indene; its purity was established by the following analysis:

0·2107 gave 0·7071 CO<sub>2</sub> and 0·1570 H<sub>2</sub>O. C = 91·5; H = 8·3.

C<sub>11</sub>H<sub>12</sub> requires C = 91·6; H = 8·3 per cent.

In order to compare its density with that of its lower homologue, indene, specific gravity determinations were made with a freshly distilled sample boiling at 234°.

The weights of water and liquid, at 4°, are 1·1444 and 1·1554 respectively, each weight being the mean of 5 determinations; the sp. gr. is 1·009 at 4°/4°.

The sp. gr. of synthetical indene, prepared in an analogous manner by Kipping and Hall (*loc. cit.*), is 1·008.

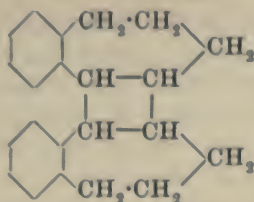
#### *Action of Various Reagents on Phenocycloheptene.*

A small quantity of the hydrocarbon does not furnish a picrate either on warming with picric acid or on mixing the two substances in benzene solution.

As indene readily condenses with benzaldehyde giving a crystalline derivative, C<sub>6</sub>H<sub>4</sub> <  $\begin{array}{c} \text{CHPh(OH)} \\ \text{CH} \end{array} \rangle \text{CH}$  (Marckwald, *Ber*, 1895, 28, 1500), it seemed desirable to see if phenocycloheptene would behave in a like manner.

This, however, does not seem to be the case, for if the hydrocarbon is warmed with benzaldehyde, even in the presence of a considerable quantity of sodium ethoxide, no reaction appears to take place, as no change in colour is observed and there is no development of heat; the product, moreover, does not solidify on standing.

On treatment with strong sulphuric acid at the ordinary temperature, the hydrocarbon passes into a pasty mass, which, on adding water, is precipitated as a heavy oil. As this product did not seem to crystallise at all readily, it was not investigated; possibly it is a condensation product having the following constitution:



Apparently, nearly the whole of the hydrocarbon is converted into this substance, and sulphonation, if it takes place at all, does so only to a limited extent.

Phenocycloheptene is not readily acted on by cold concentrated nitric acid, but on the addition of a little strong sulphuric acid nitration seems to occur, most of the hydrocarbon passing into solution; on subsequently diluting with water, a yellow solid is precipitated.

#### *Oxidation of Phenocycloheptene with Potassium Permanganate.*

In order to prove the existence of an ethylene linking in the seven-membered carbon ring of phenocycloheptene, the action of potassium permanganate was tried; it was found that a dilute neutral solution was readily reduced by a few drops of the hydrocarbon at the ordinary temperature even though the latter is practically insoluble in water.

Powdered potassium permanganate was added to the hydrocarbon suspended in water until the pink colour persisted, the solution being afterwards filtered and evaporated to a small bulk; on acidifying with hydrochloric acid, an acid was obtained which crystallised out, on cooling, in long, slender needles melting at  $122^{\circ}$ .

As under the above conditions the production of phenylbutyric-*o*-carboxylic acid, which is described by Roser (*loc. cit.*) as crystallising in plates melting at  $138^{\circ}$ , was expected, the oxidation product was recrystallised from water, dried over sulphuric acid, and analysed, the following result being obtained:

0.1188 gave 0.2764  $\text{CO}_2$  and 0.0598  $\text{H}_2\text{O}$ .  $\text{C} = 63.45$ ;  $\text{H} = 5.58$ .

$\text{C}_{11}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 63.4$ ;  $\text{H} = 5.70$  per cent.

It thus appears from the analysis that oxidation has resulted in the production of phenylbutyric-*o*-carboxylic acid; this view of the composition of the acid being confirmed by an analysis of its silver salt:

0.056 gave 0.0285 silver.  $\text{Ag} = 50.9$ .

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 51.2$  per cent.

The great difference in melting point and crystalline form between



our acid and Roser's was at first inexplicable, as in both cases the method of formation pointed emphatically to the constitution  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and isomerism was out of the question. We therefore prepared phenylbutyric-*o*-carboxylic acid by Roser's method, namely, by heating together phthalic and succinic anhydrides in presence of anhydrous sodium acetate, and, after boiling the solution of the resulting anhydride, reducing the benzoylpropionic-*o*-carboxylic acid in sealed tubes by means of hydriodic acid and phosphorus; the reduced acid thus obtained crystallised from water in shining plates, melted at  $138^\circ$ , and was apparently quite different from that obtained by the oxidation of phenocycloheptene.

It was subsequently found, however, on crystallising the acid obtained by the oxidation of the hydrocarbon, that instead of giving needles melting at  $122^\circ$  it was deposited from water in plates melting at  $138^\circ$ .

The identity of this acid with the one obtained by Roser's method was then easily established; intimate mixtures, obtained by evaporating to dryness, aqueous solutions of the acids from the two sources in various proportions, were found to melt at the same temperature as the separate components, namely, at  $138^\circ$ .

These observations seemed to show that phenylbutyric-*o*-carboxylic acid is dimorphous, and further experiments confirmed this view, inasmuch as the acid obtained by the oxidation of the hydrocarbon, when crystallised from water, sometimes gave the needles melting at  $122^\circ$  and sometimes the less fusible plates.

Wishing to make a more complete investigation of the supposed dimorphism, we tried to convert the sample prepared by Roser's method into the modification melting at  $122^\circ$ , but were unsuccessful; moreover, on oxidising a further quantity of the hydrocarbon, we were unable to get the form melting at  $122^\circ$ , the acid persistently separating from water in plates melting at  $138^\circ$ , even when the solution was crystallised at temperatures ranging from  $0^\circ$  to about  $100^\circ$ .

The same result was obtained when the acid was crystallised from water containing hydrochloric acid or potassium chloride; although, unfortunately, we have not been able to arrive at any satisfactory explanation of our failure to determine the conditions which give the substance melting at  $122^\circ$ , our experiments show exclusively that the oxidation product of phenocycloheptene is identical with Roser's phenylbutyric-*o*-carboxylic acid.

#### *Oxidation of Pheno- $\alpha$ -ketoheptamethylene with Nitric Acid.*

In a previous paper (*ibid.*), we described the results of oxidising this ketone with nitric acid, and showed that *o*-phthalic acid was one of the products thus obtained. Having a further quantity of the

ketone at our disposal, we repeated the experiment under different conditions in order to obtain phenylbutyric-*o*-carboxylic acid, and thus confirm the conclusions arrived at from the results of the oxidation of the hydrocarbon with potassium permanganate. On boiling the ketone with very dilute (about 2—3 per cent.) nitric acid, practically the whole passes into solution, and after evaporating to a small bulk, filtering, and allowing to cool, an acid crystallises out in shining plates melting at 138°.

This product is sparingly soluble in cold water and agrees in physical properties with phenylbutyric-*o*-carboxylic acid prepared by Roser's method; moreover, on evaporating aqueous solutions of mixtures of the acids in varying proportions, homogeneous solids melting at 138° are obtained.

#### *Action of Bromine on Phenocycloheptene.*

In order to demonstrate further the unsaturated character of phenocycloheptene, we attempted to prepare a dibromo-additive compound by slowly adding the theoretical quantity of bromine, in dry chloroform, to the hydrocarbon in the absence of daylight; a considerable amount of heat was developed during the process, the product being well cooled from time to time; after the whole of the bromine had been added, the solution, which was colourless, was left for several hours. The chloroform was then distilled off, but on attempting to fractionate the residue it turned dark brown, and evolved hydrogen bromide as soon as the temperature reached about 80°; even under a pressure of only 15 mm., considerable decomposition takes place, the separation of hydrogen bromide being accompanied by charring, so that only a small quantity volatilises as a thick, dark oil.

The additive compound, however, is volatile in steam, and is thus obtained in an almost colourless condition; it has then a strongly aromatic odour, and is heavier than water at the ordinary temperature. It does not solidify on cooling to 0°, whereas indene dibromide is a solid melting at 44°. Prolonged boiling with sodium carbonate solution has little or no effect on the dibromide, and digestion with dilute nitric acid apparently does not afford a crystalline oxybromide, the production of which might be expected from the ease with which indene dibromide yields a crystalline oxybromide under like conditions.

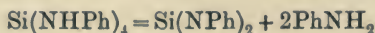
The authors desire to thank the Government Grant Committee of the Royal Society for a grant in aid of this research.

XXV.—*Researches on Silicon Compounds. Part VIII.*  
*Interactions of Silicophenylamide and Thiocarbimides.*

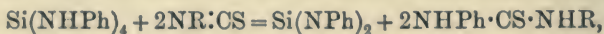
By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

THE fine crystalline silicophenylamide described in Part V of this series of papers has been shown (Trans., 1900, 77, 836) to lose aniline on careful heating and to afford, in the first instance, silicotriphenylguanidine and then silicodiphenylimide. The latter substance was also found to exist in two modifications, one being soluble, and the other insoluble, in benzene. These substances being apparently analogues of known carbon compounds, it became desirable to ascertain whether either of them could be formed by definite chemical interaction rather than by heat alone.

The comparative ease and completeness with which the change



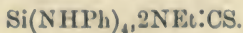
can be realised, suggested the investigation of the action of thicarbimides, or mustard oils, on the primary silicon compound. It was anticipated that silicophenylamide would interact in the following manner with a thiocarbimide,



and that the silicon diimide and symmetrical disubstituted thiocarbamide could be easily separated.

In the experimental part of this paper, it is shown that the above change can be realised, and therefore that the diimide can be formed by chemical interaction; but that, owing to the marked tendency of silicon to build up complex molecules, other and unexpected changes occur with the thiocarbimides under varying conditions. The mustard oils chiefly used were the methyl-, ethyl-, and phenyl-thiocarbimides,\* and these agree in yielding three classes of products, namely:—

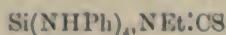
(1) Addition compounds, by simple union with silicophenylamide, when the latter and the thiocarbimide are heated together, either without or with a solvent (benzene preferably) under the atmospheric pressure. For example, ethylthiocarbimide used in excess, and dissolved in benzene, gives fine, needle-like crystals of



\* Allylthiocarbimide also interacts with silicophenylamide, but the presence of the unsaturated allyl radicle introduced a new and complicating factor which it was desirable to exclude in the first instance.

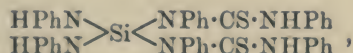


When the thiocarbimide is not in excess, the compound



is obtained in rhombic plates. Both these substances readily part with their thiocarbimide at  $100^\circ$  and leave the silicophenylamide unchanged.

(2) Compounds isomeric with those of (1), which are produced by the interaction of silicophenylamide with two molecules of thiocarbimide in pressure tubes at  $160^\circ$ . These are very viscid liquids, homogeneous to solvents, but capable of slow dissociation in boiling benzene into the insoluble modification of silicodiphenylimide and symmetrical thiocarbamide. Hence, under the conditions stated, the anticipated interaction occurs, but the products form the viscous substance  $\text{Si}(\text{NPh})_2, 2\text{NHR} \cdot \text{CS} \cdot \text{NPh}$ , which is much more difficult to dissociate than the addition compounds of the first order, but then affords a symmetrical thiocarbamide instead of a thiocarbimide. The constitution for these substances which best accords with the facts is



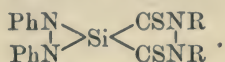
since it indicates their capacity for interaction with two additional mols. of thiocarbimide.

(3) Compounds of a third class are found to exist, which result from the interaction of silicophenylamide with four molecules of thiocarbimide at  $160$ — $170^\circ$  under pressure. The products are very viscid liquids, but they are not homogeneous, as crystals slowly separate which prove to be those of a thiocarbamide, and the proportion of the latter varies with the length of time the tubes have been heated. In these cases, it is probable that, in the earlier stages of the interactions, compounds of the second order are produced, and the further attack by excess of the thiocarbimide leads to the intermediate formation of



this product, on continued heating, breaks down (the amount of decomposition depending on the duration of the experiment) into disubstituted thiocarbamides, usually both symmetrical and unsymmetrical, and a residue which constitutes a great part of the viscid liquid. The three thiocarbimides afforded similar products when sufficiently heated, and the viscid liquids so obtained are soluble in benzene, dissociation taking place only when the intermediate compound was present, owing to imperfect action. These liquids are precipitated unchanged from their benzene solutions by ligroin; they are dissolved and decomposed by alcohol, and yield ethyl orthosilicate, alkyl dithiocarbamate, and

strongly basic substances of the guanidine type. Hence the constitution of the new silicon compound formed in each case is probably



This view is supported by the further observation that silico-diphenylimide, prepared by heat alone from silicophenylamide, combines directly with a thiocarbimide at 170—180° to form a compound having the same properties.

The general conclusion which results from this part of the investigation is that the analogies traceable between silicon and carbon in these nitrogen compounds, and the interactions which lead to their formation, are only well marked in the second class of new substances, whilst in those of the third class they almost disappear.

#### EXPERIMENTAL.

##### 1. *Addition Compounds of Silicophenylamide with Thiocarbamides.*

*Ethylthiocarbimide* was that first used, and in the proportion of two mols. to one mol. of silicophenylamide. The latter was dissolved in the smallest possible quantity of boiling benzene, the imide was then added, and the boiling continued for some time. On cooling, the liquid had no longer the odour of the thiocarbimide; more was therefore added and the solution again heated, but without effecting further combination. As no crystals separated, even on long standing in the cold, ligroin was added until the mixture became turbid, when a good crop of long, needle-like crystals gradually formed. These were removed, redissolved in benzene, again separated by ligroin, and dried over oil of vitriol. The dry crystals had a slight smell of thiocarbimide at the ordinary temperature, but the odour became very strong when they were heated at 97°, the temperature at which they begin to melt. On heating in dry hydrogen until the weight remained constant, they lost 30·16 per cent. of thiocarbimide instead of the 30·52 per cent. required by theory for  $\text{Si}(\text{NHPh})_4 \cdot 2\text{NEt} \cdot \text{CS}$ .

A determination of silicon gave 5·03 per cent. Si instead of 4·92, the sample having undoubtedly lost a little thiocarbimide while drying over oil of vitriol. So loosely is a portion of the imide held that repeated solution in benzene with precipitation by ligroin led to a very appreciable dissociation.

The mother liquor from which the above compound had separated was distilled down to a small volume and the excess of thiocarbimide partly removed along with the vapours of benzene and ligroin. The hot residual liquid was again treated with ligroin until just turbid, and then set aside. Rosettes of small needles separated after some hours,

mixed with a few of the long crystals of the first compound. The latter were picked out and the rosettes were purified by dissolving in the minimum of boiling benzene, from which, after two days, the new compound separated in small rosettes; these were rapidly washed with benzene and dried over oil of vitriol.

This compound also gives off thiocarbimide on heating, but not nearly so readily as that first obtained, consequently it is much more easily produced and kept in good condition for analysis, and the results agree closely with the formula  $\text{Si}(\text{NHPh})_4, \text{EtN}:\text{CS}$ . Theory,  $\text{Si}=5.79$ ;  $\text{N}=14.50$ . Found,  $\text{Si}=5.78$ ;  $\text{N}=14.77$  and  $14.73$ . Therefore, in presence of the solvent benzene, ethylthiocarbimide only forms addition compounds with silicophenylamide. I may add that on heating the two substances without solvent, even at the boiling point of the thiocarbimide under atmospheric pressure, there is no farther action.

*Methylthiocarbimide* yields the compound  $\text{Si}(\text{NHPh})_4, 2\text{MeN}:\text{CS}$  in short, trimetric prisms; these being most easily obtained by heating silicophenylamide without a solvent and at the ordinary pressure. Combination is easily effected by this means, and the new compound is best obtained by dissolving the product in the least possible volume of hot benzene, and then adding ligroin gradually until a slight turbidity is obtained; the crystals slowly separate on cooling. This compound is quite as easily decomposed by heat as that obtained from ethylthiocarbimide.

From phenylthiocarbimide, the compound  $\text{Si}(\text{NPh})_2, 2\text{NPh}:\text{C}:\text{S}$  is produced by the treatment described above, and is obtained in crystals which are apparently monoclinic prisms.

## 2. Interactions of Silicophenylamide with Two Molecules of Thiocarbimides.

As the heating together of silicophenylamide with a thiocarbimide, either in the presence of solvents or without solvents at the ordinary pressure, led merely to the production of addition compounds, the next experiments were made in sealed tubes. Two mols. of *ethylthiocarbimide* and one of silicophenylamide were sealed up and carefully heated in a glycerol bath. The contents of the tube, when liquefied, were heated at  $140^\circ$ , and a change commenced, leading to the formation of a yellow liquid, which increased in amount as the temperature rose to  $160^\circ$ . Half an hour's heating at  $160^\circ$  completed the reaction. On cooling, the material became syrupy, and when cold the contents consisted of a clear and very viscid liquid quite free from the odour of thiocarbimide, even on warming. It was therefore evident that a definite interaction had taken place.



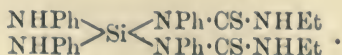
A portion of this liquid was sealed up in a tube and kept for several months, but it did not exhibit any tendency to crystallise, and seemed perfectly homogeneous. To the remainder, benzene was added, the two liquids being freely miscible, but slow evaporation of a part of the solution did not furnish crystals, and only an oily residue was left. Again, ligroin, when added gradually to the benzene solution, only caused the separation of oily droplets, and by the addition of sufficient ligroin the whole of the product was precipitated as a heavy and viscid liquid layer. A repetition of the treatment proved to be the best mode of purifying the material from the small proportion of secondary products which formed during the interaction. When so purified, and gently heated to expel any benzene and ligroin, the very viscid and slightly yellow liquid was found to act with indifferent solvents as a homogeneous substance. The percentage of silicon was determined and proved to be  $\text{Si} = 4.96$ , or practically the same as that of the addition compound,  $\text{Si}(\text{NPh})_4 \cdot 2\text{EtN} \cdot \text{CS}$ , already described. The two substances are therefore isomeric, but very different in properties.

Attempts were then made to effect the dissociation of the viscid liquid, and the problem was solved by the prolonged digestion of the substance in ten volumes of boiling benzene.

Under these conditions, a gelatinous substance gradually separated, which, when collected, washed well with benzene, and dried, was found to contain  $\text{Si} = 13.35$  per cent., theory for  $\text{Si}(\text{NPh})_2$  being  $\text{Si} = 13.33$  per cent. Silicodiphenylimide, in its insoluble modification, is therefore one of the products of dissociation, and the marked tendency of the silicon diimide to pass into the modification insoluble in benzene facilitates the change.

The benzene solution, when concentrated and filtered from some more diimide, yielded crystals on cooling. These were collected and purified by solution in ether, from which they were obtained in the beautiful plates characteristic of symmetrical phenylethylthiocarbamide. They melted at  $101^\circ$  and gave the usual reaction of a thiocarbamide with alkaline lead tartrate.

Therefore, by the interaction of 1 mol. of silicophenylamide with 2 mols. of ethylthiocarbimide at  $160^\circ$ , the anticipated interaction was ultimately realised, but it was complicated by the intermediate formation of a new and tolerably stable substance, which may be represented by the formula  $\text{Si}(\text{NPh})_2 \cdot 2\text{EtHN} \cdot \text{CS} \cdot \text{NPh}$ , but more probably has the following constitution :



The new substance has the same percentage composition as the addition

compound of the first order, and, like the latter, is dissociated in boiling benzene, though much more slowly and into wholly different products.

*Methyl-* and *phenyl-thiocarbimides* were found to yield viscid liquids of similar composition, which dissociate in the same manner. The phenyl mustard oil necessarily produced thiocarbanilide as the symmetrical thiocarbamide resulting from the change.

It is evident that compounds having the constitution represented by the second of the above formulæ should be able to interact with two additional molecules of thiocarbimide and yield  $\text{Si}(\text{NR}\cdot\text{CS}\cdot\text{NHPb})_4$ .

### 3. *Interaction of Silicophenylamide with excess of Thiocarbimides.*

In addition to the considerations mentioned at the end of the last section it was noticed that the substance resulting from the interaction of the silicon compound at  $160^\circ$  with two mols. of the imide gave evidence of the presence of secondary products. It was also noticed in preliminary experiments that, when a distinct excess over two molecules of thiocarbamide was used, the whole of the latter disappeared and the secondary products were present in still larger proportions in the liquids removed from the pressure tubes. Direct observations, therefore, indicated that silicophenylamide could combine with more than two molecules of thiocarbimide, and the results of small experiments left no doubt that sufficiently prolonged heating under pressure led to the disappearance of four molecules of a mustard oil. It was also found that the products of interaction with methylthiocarbimide were rather less difficult to separate, hence I shall describe the treatment adopted in the largest experiment made with that substance.

Pure crystallised methylthiocarbimide (18 grams) and 24 grams of silicophenylamide (4 : 1 mols.) were sealed up in a pressure tube, which was then gradually heated in a glycerol bath. The methyl compound speedily melted and dissolved the silicophenylamide, and complete liquefaction was obtained with perfect mixture. A portion of the tube projected outside the bath, and in this the volatile thiocarbimide condensed and dropped back into the liquid. As the interaction proceeded, this condensation diminished, and after heating at  $170$ — $180^\circ$  for three hours it practically ceased. The tube and its contents were allowed to cool overnight; when cold, the material resembled that already described in the second section, but the very viscid product was not homogeneous, as crystals, which subsequently proved to be those of separated thiocarbamide, slowly formed throughout the somewhat yellow, and nearly solid, mass. When the tube was opened, there was a slight odour of uncombined thiocarbimide with that of methyl sulphide.

The contents of the tube were then liquefied by heat and allowed to flow into a flat-bottomed flask, in which they were further warmed to expel volatile matter.

In a former experiment, it was found that the direct separation of the thiocarbamide could be effected by dissolving the product from the tube in benzene, precipitating nearly all the viscid substance by addition of sufficient ligroin, pouring off the supernatant liquid, and allowing it to stand for a day, when the thiocarbamide which crystallised out was easily purified by repeated crystallisation from alcohol. The thick liquid, when purified by redissolving in benzene and fractional precipitation by ligroin, ultimately gave a product which contained Si = 8.02 per cent. and was easily decomposed by solution in alcohol.

Taking advantage of the knowledge of these facts, and considering that the products of decomposition of the viscid liquid by alcohol would probably afford the best evidence of the constitution of the new substance, the whole of the material from the present experiment was at once dissolved in hot alcohol, in which it was completely soluble. The solution was digested for several hours so as to secure the conversion of silicon into ethyl silicate. The alcohol was then distilled off, carrying with it compounds derived from the dithiocarbamates probably formed during the treatment. The residue was digested with aqueous alcohol, and hydrated silica separated as a product of the hydrolysis of the ethyl silicate. When the hydrate was completely removed, the filtered solution was found to be strongly alkaline. The basic substance was just neutralised by hydrochloric acid and the liquid then largely diluted with water. In this way, any substituted thiocarbamide present was precipitated, while the hydrochloride of the base remained in solution. The basic substance was precipitated in an amorphous state by sodium hydroxide, but its solution in alcohol furnished botryoidal groups of crystals which melted at 140°. This, and similar bases produced in the other interactions, will be fully described later on.

The pure base gave N = 15.13 per cent. The formula  $C_{15}H_{23}N_3$  requires 14.95 per cent.

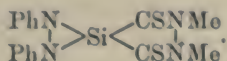
It afforded a fine platinichloride easily purified by crystallisation; this gave Pt = 19.11 per cent. The formula  $(C_{15}H_{23}N_3)_2H_2PtCl_6 \cdot 2H_2O$  requires Pt = 19.32 per cent.

This substituted guanidine gives a hydrochloride which crystallises well. Like all the guanidines, it forms a readily fusible picrate by which, owing to its low solubility, it can be separated from dilute solutions of the salts.

It is therefore probable that when silicophenylamide is heated at 170—180° with excess of methylthiocarbamide the compound



$\text{Si}(\text{NPh}\cdot\text{CS}\cdot\text{NHR})_4$  is formed, but this gradually breaks down by long continued heating into a disubstituted thiocarbamide and the final viscid substance, which gave  $\text{Si} = 8.02$  per cent.,  $7.87$  per cent. being required by the formula



The products afforded by the alcoholic decomposition of the oily compound accord with this view of its constitution.

Moreover, a liquid substance possessing the same properties was formed by heating at  $170\text{--}180^\circ$  for three hours, two mols. of the thiocarbimide with 1 mol. of silicodiphenylimide, which latter had been independently prepared in the first instance by heating silicophenylamide in a current of dry hydrogen until 2 mols. of aniline had been removed.

*Ethylthiocarbimide* and *phenylthiocarbimide*, when heated in excess with silicophenylamide, afforded products similar to that obtained with methylthiocarbimide, but the experiments performed with them were not made with such comparatively large quantities of materials as were used in the case of the work with methylthiocarbimide. In each instance, guanidines also result from the alcoholic decomposition of the new silicon compounds.

## XXVI.—*The Influence of Molybdenum and Tungsten Trioxides on the Specific Rotations of l-Lactic Acid and Potassium l-Lactate.*

By GEORGE GERALD HENDERSON and JAMES PRENTICE.

It has been shown by Henderson and Prentice (Trans., 1902, 81, 658) that the changes in the rotation of a solution of potassium *l*-lactate which are produced by the dissolution of increasing quantities of arsenious oxide or boric oxide point to the formation of potassium arseniolactate,  $\text{CH}_3\cdot\text{CHO}(\text{AsO})\cdot\text{CO}_2\text{K}$ , and potassium borolactate,  $\text{CH}_3\cdot\text{CHO}(\text{BO})\cdot\text{CO}_2\text{K}$ , respectively. It has also been shown that evidence of the existence of arsenio- and boro-lactic acids is obtained by observation of the rotations of solutions of the oxides in *l*-lactic acid. Corresponding experiments have now been made with molybdenum and tungsten trioxides, and results have been obtained which prove that these oxides react with potassium lactate in aqueous solution to form a molybdilactate and a tungstilactate of potassium respectively, the composition of which may be represented by the

formula  $\text{RO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2$ . Further, it has been found that when sodium molybdate or sodium tungstate is dissolved in an aqueous solution of lactic acid, sodium salts corresponding to the above potassium salts are produced, and that molybdenum trioxide and lactic acid interact in aqueous solution with formation of a substance in which 1 mol. of  $\text{MoO}_3$  is combined with 1 mol. of  $\text{C}_3\text{H}_6\text{O}_3$ .

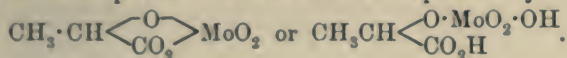
Molybdenum trioxide is readily dissolved, under suitable conditions, by a warm aqueous solution of potassium *l*-lactate. The specific rotation increases with the quantity of oxide in solution, and reaches a maximum when the substances are present in the proportion of 2 mols. of lactate to 1 mol. of oxide, that is to say, in the quantities necessary for the formation of potassium molybdilactate according to the equation  $2\text{C}_3\text{H}_5\text{O}_3\text{K} + \text{MoO}_3 = \text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2 + \text{H}_2\text{O}$ . The yellowish solution of this compound may be kept without undergoing change, but if a small additional quantity of molybdenum trioxide is dissolved in it the liquid acquires a blue colour and gives a crystalline deposit after a short time. Tungsten trioxide is also dissolved, though with much greater difficulty, by a hot aqueous solution of potassium *l*-lactate. The specific rotation increases slowly as the quantity of oxide in solution is increased, and the highest reading is obtained when the substances are present in the proportion corresponding with the equation  $2\text{C}_3\text{H}_5\text{O}_3\text{K} + \text{WO}_3 = \text{WO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2 + \text{H}_2\text{O}$ . No more than a trace of oxide in excess of this quantity passes into solution, whatever be the concentration of the lactate, and thus the formation of a definite compound, potassium tungstilactate, is indicated.

Sodium molybdate and the corresponding tungstate both dissolve readily in an aqueous solution of *l*-lactic acid. In each case, the specific rotation, which increases as more salt is added, reaches a maximum when 1 mol. of molybdate or tungstate is present for each 2 mols. of lactic acid, and diminishes on addition of larger quantities of the salt. These results show that the following reaction has occurred in each case,  $2\text{C}_3\text{H}_6\text{O}_3 + \text{Na}_2\text{RO}_4 = \text{RO}_2(\text{C}_3\text{H}_4\text{O}_3\text{Na})_2 + 2\text{H}_2\text{O}$ , hence that molybdi- and tungsti-lactates are formed by the interaction of lactic acid with molybdates and tungstates as well as by the action of molybdenum and tungsten trioxides on lactates.

An aqueous solution of *l*-lactic acid dissolves molybdenum trioxide in the cold, but the compound formed is unstable when exposed to light, and the liquid quickly acquires a blue colour unless kept in the dark. When increasing quantities of the oxide are dissolved, the specific rotation also increases until 2 mols. of  $\text{MoO}_3$  are present for each 2 mols. of  $\text{C}_3\text{H}_6\text{O}_3$ , but diminishes if more oxide is added. The point at which the specific rotation reaches its highest value corresponds with the formation of a compound  $\text{MoO}_2 \cdot \text{C}_3\text{H}_4\text{O}_3$  or  $\text{MoO}_2(\text{OH}) \cdot \text{C}_3\text{H}_5\text{O}_3$ . On the other hand, tungsten trioxide was found to be so sparingly

soluble in a solution of *l*-lactic acid that it was useless to determine the rotation.

The chief interest of the results described in this, as well as in the previous paper (*loc. cit.*), lies in the fact that they are in accordance with the views regarding the constitution of compounds of the "tartar emetic" type, which have been fully stated in a former communication to the Society (Trans., 1899, 75, 542) and therefore need not be recapitulated here. It is sufficient to note that, according to these views, molybdenum and tungsten trioxides should react with lactates to form compounds of the formula  $\text{RO}_2(\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{M})_2$ , and that it is precisely compounds of this composition the formation of which is inferred from the study of the specific rotations of solutions of the oxides in potassium *l*-lactate, and of solutions of sodium molybdate and sodium tungstate in *l*-lactic acid. As regards the compound formed by dissolving molybdenum trioxide in *l*-lactic acid, its most probable constitution is expressed by either of the formulæ



#### EXPERIMENTAL.

##### *Molybdenum Trioxide and Potassium l-Lactate.*

Some trouble was experienced in preparing a solution of molybdenum trioxide in aqueous potassium *l*-lactate suitable for observation in the polarimeter, because if the mixture was boiled, or if the oxide was added to a hot solution of the lactate, the liquid acquired a blue colour, which rendered determinations of the rotation impossible. This difficulty was overcome by adding the oxide to a cold normal solution of the lactate, gradually warming the mixture on a water-bath and heating until all the oxide had dissolved. Under these conditions, no blue coloration appeared, but when nearly saturated with the oxide the liquid became yellow; in this way, a number of solutions containing from 1/4 mol. to 1 mol. of  $\text{MoO}_3$  for each 2 mols. of  $\text{C}_3\text{H}_5\text{O}_5\text{K}$  were prepared. A still larger proportion of molybdenum trioxide could be dissolved in the hot solution, but if this was done the liquid always became dark blue and also gave a crystalline deposit on cooling, even when the solution of the lactate was diluted to one-fifth of its original strength. Observations of the rotation were made after each addition of the oxide, and the results, which are given in the following table, showed that the maximum rotation was reached when the oxide was present in sufficient quantity to form potassium molybdilactate,  $\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2$ , by reaction with the lactate.

In all the following experiments, a 2 dm. polarimeter tube was used,



and the observations were made at 20°. Some of the experiments were made with *d*- and others with *l*-lactic acids or their salts, but for simplicity the results have been stated in all the tables as if *l*-lactic acid or potassium *l*-lactate had been used in every case:

| Weight of $C_3H_5O_3K$ in 25 c.c. of solution. | Weight of $MoO_3$ added. | Molecular proportions of $C_3H_5O_3K$ and $MoO_3$ . | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . |
|--|--------------------------|---|-------------------------|---------------------------|
| 3.2025   | —                        | 2 : 0   | +2.58°                  | +10.95°                   |
| "  | 0.45                     | 2 : 0.25  | 4.19                    | 14.33                     |
| "  | 0.90                     | 2 : 0.50  | 5.84                    | 17.77                     |
| "  | 1.35                     | 2 : 0.75  | 7.50                    | 20.58                     |
| "  | 1.62                     | 2 : 0.90  | 8.44                    | 21.87                     |
| "  | 1.80                     | 2 : 1.00  | 9.09                    | 22.69                     |

It was found that dilution has no perceptible effect on the specific rotation of a solution of potassium molybdilactate containing 1 mol. of  $MoO_3$  to 2 mols. of  $C_3H_5O_3K$ , but that alteration of temperature causes a considerable change, as is evident from the following figures:

| Temperature.            | 15°.   | 20°.   | 40°.    |
|-------------------------|--------|--------|---------|
| $\alpha_D^{20^\circ}$   | +8.55° | +9.09° | +10.55° |
| $[\alpha]_D^{20^\circ}$ | 21.35  | 22.69  | 26.35   |

#### *Tungsten Trioxide and Potassium l-Lactate.*

In order to obtain potassium tungstilactate, a normal solution of potassium *l*-lactate was heated on a water-bath and tungsten trioxide gradually added in small quantities. The oxide was not dissolved at all readily even on somewhat prolonged heating of the liquid, especially as the quantity in solution increased, but ultimately several solutions were prepared which contained from 1/4 mol. to 1 mol. of  $WO_3$  for each 2 mols. of  $C_3H_5O_3K$ . As in the case of molybdenum trioxide, the experiments had then to be interrupted, because no more than a trace of the oxide in excess of 1 mol. could be dissolved, whether the solution of the lactate was concentrated or dilute. Moreover, up to this point, the liquid remained colourless, but the presence of even a very small additional quantity of the oxide produced a brown coloration which made it impossible to determine the rotation. It was found that the rotation reached a maximum when the quantities of the substance necessary for the formation of potassium tungstilactate,  $WO_2(C_3H_4O_3K)_2$ , were present—an exactly similar result to that obtained in the experiments with molybdenum trioxide. The observations are given in the following table; it will be noticed that,

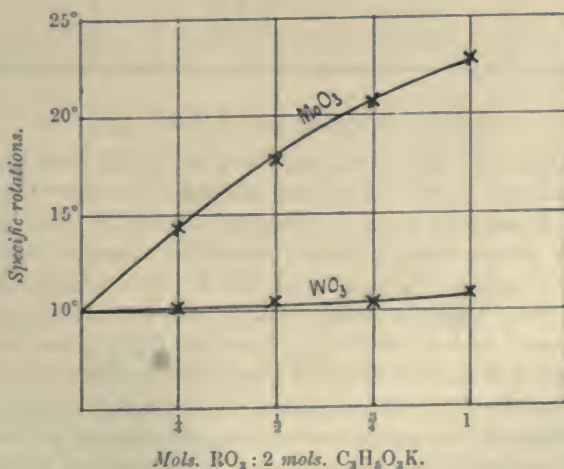
whilst the rotation of the solution increases steadily with increase in the quantity of tungsten trioxide present, the specific rotation remains almost stationary :

| Weight of $C_3H_5O_3K$ in 25 c.c. of solution. | Weight of $WO_3$ added. | Molecular proportions of $C_3H_5O_3K$ and $WO_3$ . | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . |
|--|-------------------------|--|-------------------------|---------------------------|
| 3.2025   | —                       | 2 : 0  | +2.58°                  | +10.05°                   |
| "  | 0.725                   | 2 : 0.25   | 3.19                    | 10.14                     |
| "  | 1.450                   | 2 : 0.50   | 3.86                    | 10.36                     |
| "  | 2.175                   | 2 : 0.75   | 4.42                    | 10.27                     |
| "  | 2.610                   | 2 : 0.90   | 4.81                    | 10.34                     |
| "  | 2.900                   | 2 : 1.00   | 5.27                    | 10.80                     |

The specific rotation of the solution of potassium tungstilactate containing 1 mol. of  $WO_3$  to 2 mols. of  $C_3H_5O_3K$  was found to be practically unaffected by dilution, but that it varies with temperature is shown by the following results :

| Temperature.            | 15°.   | 20°.   | 40°.   |
|-------------------------|--------|--------|--------|
| $\alpha_D^{20^\circ}$   | +4.84° | +5.27° | +6.49° |
| $[\alpha]_D^{20^\circ}$ | 9.91   | 10.80  | 13.29  |

The changes in the specific rotation of potassium *l*-lactate by the dissolution of molybdenum and tungsten trioxides in a normal solution are clearly illustrated if the results are stated graphically :



*Sodium Molybdate and l-Lactic Acid.*

The solutions employed in the polarisation determinations were prepared by dissolving sodium molybdate in water in such quantity that 1 c.c. of the solution contained 0.05 gram of salt. The required amount of the solution was added to a measured quantity of a normal solution of *l*-lactic acid, the mixture concentrated on a water-bath and, when cool, transferred to a small graduated flask, which was filled up to the mark with the washings of the evaporating basin. The solutions thus prepared were perfectly colourless, and no crystals separated, even when they were kept for a long time. The observations of the rotation, which are given in the table below, showed that the maximum was reached when the solution contained 1 mol. of  $\text{Na}_2\text{MoO}_4$  to 2 mols. of  $\text{C}_3\text{H}_6\text{O}_3$ , and that any increase in the quantity of the salt beyond this point caused a diminution of the specific rotation. This result pointed to the formation of sodium molybdilactate according to the equation  $2\text{C}_3\text{H}_6\text{O}_3 + \text{Na}_2\text{MoO}_4 = \text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{Na})_2 + 2\text{H}_2\text{O}$ :

| Weight of $\text{C}_3\text{H}_6\text{O}_3$ in 25 c.c. of solution. | Weight of $\text{Na}_2\text{MoO}_4$ added. | Molecular proportions of $\text{C}_3\text{H}_6\text{O}_3$ and $\text{Na}_2\text{MoO}_4$ . | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . |
|--|--|---|-------------------------|---------------------------|
| 2.25   | —  | 2 : 0   | -0.34°                  | -1.88°                    |
| "  | 0.6438                                     | 2 : 0.25  | +1.85                   | +7.99                     |
| "  | 1.2875                                     | 2 : 0.50  | 4.04                    | 14.23                     |
| "  | 1.9313                                     | 2 : 0.75  | 6.31                    | 18.86                     |
| "  | 2.3715                                     | 2 : 0.90  | 7.60                    | 20.80                     |
| "  | 2.5750                                     | 2 : 1.00  | 8.17                    | 21.15                     |
| "  | 2.8325                                     | 2 : 1.10  | 8.17                    | 20.09                     |
| "  | 3.2188                                     | 2 : 1.25  | 8.17                    | 18.67                     |

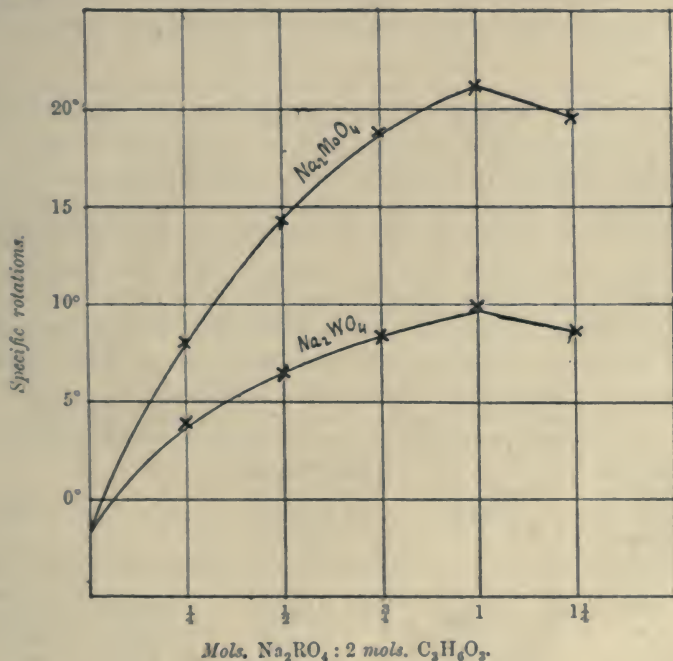
*Sodium Tungstate and l-Lactic Acid.*

The solutions of sodium tungstate in *l*-lactic acid were prepared in a similar manner to those of sodium molybdate, except that the acid used was of one-fifth normal strength, because it was found that with more concentrated solutions crystalline deposits were formed when more than a small quantity of the salt was added. As in the case of the molybdate, the specific rotation was greatest when the solution contained 1 mol. of  $\text{Na}_2\text{WO}_4$  to 2 mols. of  $\text{C}_3\text{H}_6\text{O}_3$ , and an increase in the quantity of the salt caused a diminution in the rotation. Hence the formation of sodium tungstilactate,  $\text{WO}_2(\text{C}_3\text{H}_4\text{O}_3\text{Na})_2$ , was indicated, and the results of the corresponding experiments with sodium molybdate were corroborated. The following table contains details of the experiments:



| Weight of $C_3H_5O_3$ in 25 c.c. of solution. | Weight of $Na_2WO_4$ added. | Molecular proportions of $C_3H_5O_3$ and $Na_2WO_4$ . | $\alpha_D^{20}$ . | $[\alpha]_D^{20}$ . |
|---|-----------------------------|---|-------------------|---------------------|
| 0.45  | —                           | 2 : 0   | —                 | -2.00°              |
| "   | 0.1838                      | 2 : 0.25  | +0.20°            | +3.99               |
| "   | 0.3675                      | 2 : 0.50  | 0.42              | 6.46                |
| "   | 0.5513                      | 2 : 0.75  | 0.66              | 8.23                |
| "   | 0.6615                      | 2 : 0.90  | 0.79              | 8.88                |
| "   | 0.7350                      | 2 : 1.00  | 0.94              | 9.90                |
| "   | 0.8085                      | 2 : 1.10  | 0.94              | 9.34                |
| "   | 0.9188                      | 2 : 1.25  | 0.94              | 8.58                |

The effect of adding increasing quantities of sodium molybdate or sodium tungstate to solutions of *l*-lactic acid is shown by the following curves :



#### *Molybdenum Trioxide and l-Lactic Acid.*

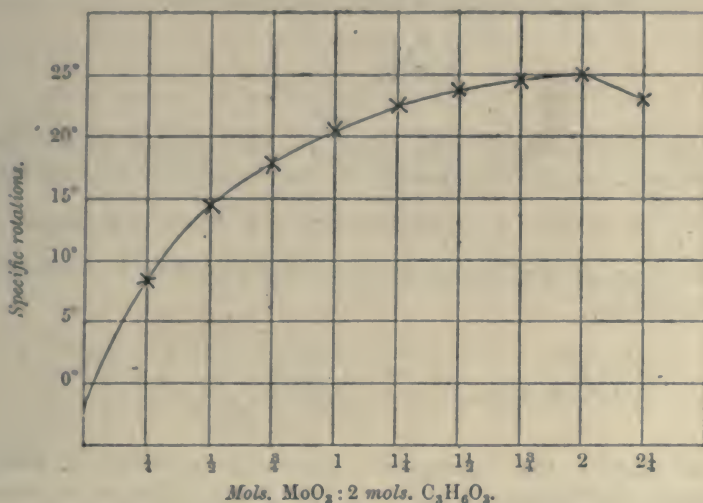
Considerable difficulty was experienced in preparing solutions of molybdenum trioxide in *l*-lactic acid, for whilst the dissolution of the oxide takes place fairly easily, even in the cold, the compound which is formed is very sensitive to the action of light, and the solution, after

a short exposure to diffused daylight, acquires a blue colour, a similar decomposition occurring on warming. It was therefore necessary to proceed as follows. After each addition of the calculated quantity of molybdenum trioxide, the flask containing the solution of lactic acid was placed in a dark cupboard and shaken up at intervals until the oxide was wholly dissolved. Colourless solutions were thus obtained, but, owing to the readiness with which a blue coloration was produced, one quantity of acid did not serve for more than one or two experiments. A seminormal solution of the acid was used for the earlier experiments, but was replaced in the later ones by a one-fifth normal solution, because the oxide was dissolved with greater difficulty as the quantity in solution increased. As will be seen from the results given in the following table, the specific rotation increased with each addition of molybdenum trioxide until 2 mols. of  $\text{MoO}_3$  were present for each 2 mols. of  $\text{C}_3\text{H}_6\text{O}_3$ , but diminished when a larger quantity of the oxide was added. Evidence was thus obtained of the formation of a definite compound of molybdenum trioxide and lactic acid.

The molybdenum trioxide used in the experiments with potassium *l*-lactate was prepared by decomposing ammonium molybdate with dilute nitric acid, evaporating to dryness several times with nitric acid, thoroughly washing the residual oxide, and then drying it in air. When prepared in this way, the oxide was very sparingly soluble in lactic acid, and therefore, in the experiments with the acid, the evaporation with nitric acid was omitted. However, under these conditions, even after prolonged washing, the oxide persistently retained traces of ammonium salts, and therefore the rotations given in the table are not absolutely, but only relatively, accurate, although the figures are certainly not far from the truth :

| Weight of $\text{C}_3\text{H}_6\text{O}_3$ in 25 c.c. of solution. | Weight of $\text{MoO}_3$ added. | Molecular proportions of $\text{C}_3\text{H}_6\text{O}_3$ and $\text{MoO}_3$ . | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . |
|--|---------------------------------|--|-------------------------|---------------------------|
| 1.125  | —                               | 2 : 0  | -0.187°                 | -2.01°                    |
| "  | 0.225                           | 2 : 0.25   | +0.89                   | +8.24                     |
| "  | 0.450                           | 2 : 0.50   | 1.81                    | 14.37                     |
| "  | 0.675                           | 2 : 0.75   | 2.59                    | 17.95                     |
| "  | 0.900                           | 2 : 1.00   | 3.31                    | 20.43                     |
| "  | 1.125                           | 2 : 1.25   | 4.01                    | 22.25                     |
| 0.45   | 0.54                            | 2 : 1.50   | 1.88                    | 23.70                     |
| "  | 0.63                            | 2 : 1.75   | 2.12                    | 24.57                     |
| "  | 0.72                            | 2 : 2.00   | 2.32                    | 24.78                     |
| "  | 0.81                            | 2 : 2.25   | 2.32                    | 23.03                     |

The curve shows these results in graphical form :



The sensibility to light of the solution of molybdenum trioxide in lactic acid led us to use it for taking a print from a negative, and the attempt was quite successful, for a good print was obtained on filter paper soaked in the solution and then dried in the dark. The blue colour faded away, however, if the print was kept in the dark for some time.

We propose to endeavour to isolate some of the compounds the existence of which is indicated by the experiments described in this paper.

CHEMICAL LABORATORY,

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

## XXVII.—*Formation of Carbazoles by the Interaction of Phenols, in the Orthoketonic Form, with Arylhydrazines.*

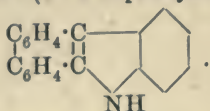
By FRANCIS R. JAPP, F.R.S., and WILLIAM MAITLAND, B.Sc.

JAPP AND FINDLAY (Trans., 1897, 71, 1117) showed that 9-hydroxyphenanthrene ("phenanthrone")\*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{OH} \end{array}$  interacts with

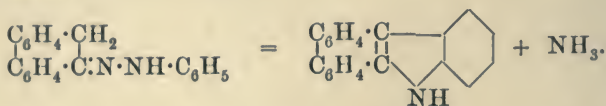
\* Werner and Frey (*Annalen*, 1902, 321, 29) describe as new, certain derivatives of 9-hydroxyphenanthrene (they prefer to call it "10-hydroxyphenanthrene")



phenylhydrazine at 200°, eliminating water and ammonia and yielding 9 : 10-phenanthrocarbazole \* (2' : 3'-diphenyleneindole)



The reaction probably takes place in two stages: in the first, 9-hydroxyphenanthrene interacts in the tautomeric ketonic form,  $\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4$ , to yield a phenylhydrazone (not isolated) which, in the second stage, parts with ammonia and is converted into 9 : 10-phenanthrocarbazole :



The reaction thus corresponds with that in which E. Fischer obtained 2' : 3'-diphenylindole from the phenylhydrazone of deoxybenzoin :

which had already been prepared by Japp and Findlay (*loc. cit.*) : namely the acetyl derivative, the methyl ether, and the picrate.

Julius Schmidt and Max Strobel (*Ber.*, 1901, **34**, 1461), and Pschorr and Schröter (*ibid.*, p. 2726) are, in like manner, apparently unaware that 9-aminophenanthrene ( $\beta$ -phenanthrylamine) has already been described by Japp and Findlay (*loc. cit.*, p. 1123).

As all these compounds are to be found in M. M. Richter's *Lexikon der Kohlenstoff-Verbindungen*, one is forced to the conclusion that this valuable work is not consulted quite so frequently as it ought to be in the country of its origin.

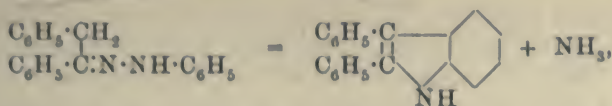
\* The nomenclature of the carbazoles adopted in the present paper is that proposed by Graebe (*Ber.*, 1894, **27**, 3066). If a carbazole contains, in place of one phenylene group, a naphthylene, phenanthrylene, or other similar group, the class name carbazole receives the prefix *naphtho*, *phenanthro*, or the like ; and if both phenylenes are so replaced, *dinaphtho* and the like must be used if the two groups are identical, *phenanthro-naphtho* and the like if they are different.

In writing the formulæ, the more complex of these bivalent groups is placed towards the left, and its positions are indicated by ordinary numerals ; those of the right hand group, where this is necessary, by accented numerals. The first of each pair of numerals refers to carbon, the second to nitrogen.

As an illustration of the application of these rules we may take

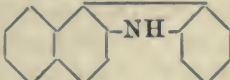


which would receive the name 9 : 10-phenanthro-2' : 1'-naphthocarbazole.



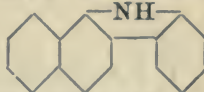
except that, in the latter case, zinc chloride was employed to bring about the elimination of ammonia (*Annalen*, 1886, 236, 135).

The foregoing considerations led us to try whether 2-naphthol, which in many respects resembles 9-hydroxyphenanthrene, would also interact in the ketonic form with phenylhydrazine to yield a naphthocarbazole. On heating 2-naphthol with excess of phenylhydrazine no reaction took place, but on adding to the mixture some dry phenylhydrazine hydrochloride and continuing the heating, water and ammonia were

evolved, and a fair yield of 1 : 2-naphthocarbazole 

(m. p. 134—135°)\* was obtained. The hydrochloric acid of the hydrochloride thus to some extent plays the part of the zinc chloride in E. Fischer's reaction.

2-Naphthol, when heated with dry phenylhydrazine hydrochloride alone, does not yield any carbazole derivative; but we succeeded in isolating from the product of the reaction *phenyl-2-naphthylamine*.

1-Naphthol, when heated with the mixture of phenylhydrazine and its hydrochloride, yielded 2 : 1-naphthocarbazole, 

(m. p. 225·5°), already obtained by Kym (*Ber.*, 1890, 23, 2465) by desulphurising thiophenyl-1-naphthylamine with finely divided copper. 1-Naphthol, however, does not appear to interact so readily in the ketonic form as 2-naphthol, and the yield of the carbazole in the present reaction is small.

Other carbazoles were prepared by the interaction of 1-naphthylhydrazine and of 2-naphthylhydrazine, together with their hydrochlorides, on 2-naphthol and on 9-hydroxyphenanthrene.

Neither phenol itself, nor thymol, gave any trace of a carbazole when heated with a mixture of phenylhydrazine and its hydrochloride. The monohydric phenols derived from benzene and its homologues are evidently incapable of taking part in this reaction.

Both resorcinol and phloroglucinol, on the other hand, react violently when heated with the foregoing mixture; but nothing definite could be isolated from the resinous products. That definite compounds—not, however, of the carbazole class—may be obtained by the action of phenylhydrazine alone on these two polyhydric phenols has been shown by von Baeyer and Kochendoerfer (*Ber.*, 1889, 22, 2189).

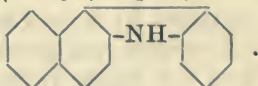
\* As regards this melting point, see the experimental part of this paper.

It appears, therefore, that in the present reaction phenol is incapable of assuming the orthoketonic form, whilst 1-naphthol assumes it with difficulty, and 2-naphthol and 9-hydroxyphenanthrene with relative ease.

We would point out that this is precisely the order of reactivity in the orthoketonic form which Thiele's very remarkable theory of double bonds would, in its application to benzene derivatives (*Annalen*, 1899, 306, 87), predict for these phenols. It would take too long to explain in detail how these results may be deduced from the theory: we will content ourselves with mentioning that they may be arrived at from a consideration of the number of "unsaturated residual affinities" and "partially saturated residual affinities" which Thiele's formulæ show in the case of the phenolic and orthoketonic (*i.e.* containing the group  $\text{CO}\cdot\text{CH}_2$ ) forms respectively of these various phenols. (See Thiele's paper, pp. 129 and 138). In these formulæ\* phenol itself appears as a saturated compound, whilst its orthoketonic form is unsaturated; 1-naphthol is unsaturated, but considerably less so than its orthoketonic form; 2-naphthol and 9-hydroxyphenanthrene again are less saturated than 1-naphthol and not much more saturated than their orthoketonic forms. The relative stabilities of any two forms are, of course, in the ratio of their degrees of saturation.

#### EXPERIMENTAL.

##### 1 : 2-Naphthocarbazole (*Phenyl-β-naphthylcarbazole*),



—Thirteen grams of 2-naphthol, 20 grams of phenylhydrazine, and 10 grams of phenylhydrazine hydrochloride were heated in an atmosphere of hydrogen in a flask fitted with a condensing tube. When the temperature of the bath reached 155—160°, a vigorous reaction took place; water and ammonia were given off; and an oil containing phenylhydrazine distilled over, mixed with the water. When the action had subsided, the temperature was raised to 170° and kept there for an hour, after which the reddish-brown pasty mass was allowed to cool in the atmosphere of hydrogen, then dissolved in hot glacial acetic acid and reprecipitated by the addition of water. The resinous substance thus obtained was dissolved in ether, and the solution was extracted first with dilute hydrochloric acid, and then with a solution of sodium hydroxide, after which it was dried with calcium chloride. On expelling the ether, a crystalline mass remained,

\* Some of the formulæ are not given by Thiele, but those which are wanting can be constructed without difficulty from the examples which he provides.



which was purified by recrystallisation from benzene, from which it was deposited in tufts of needles with a pinkish tinge. By recrystallisation from light petroleum ("ligroin") the substance was obtained in a colourless state. It melted at  $134-135^{\circ}$ . On analysis it gave figures agreeing with the formula of 1:2-naphthocarbazole.

0.1637 gave 0.5288  $\text{CO}_2$  and 0.0762  $\text{H}_2\text{O}$ .  $\text{C} = 88.10$ ;  $\text{H} = 5.17$ .

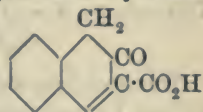
0.2104 ,, 11.5 c.c. moist nitrogen at  $13^{\circ}$  and 762 mm.  $\text{N} = 6.48$ .

$\text{C}_{16}\text{H}_{11}\text{N}$  requires  $\text{C} = 88.48$ ;  $\text{H} = 5.07$ ;  $\text{N} = 6.45$  per cent.

A pine chip, moistened with an alcoholic solution of the substance, turns violet when acted on by gaseous hydrogen chloride.

The foregoing 1:2-naphthocarbazole is identical with that obtained by Schöpf (Ber., 1896, 29, 269) by the elimination of carbon dioxide from 1:2-naphthocarbazole-3-carboxylic acid, and asserted by him to melt at  $120^{\circ}$ . F. Ullmann (Ber., 1898, 31, 1697), who afterwards prepared this compound by heating phenylazimidonaphthalene (m. p.  $149^{\circ}$ ), found the melting point at  $134.5^{\circ}$ , with which our determination agrees. He also prepared the substance by Schöpf's method and showed that the product also melted at  $134.5^{\circ}$  instead of, as stated by Schöpf, at  $120^{\circ}$ .\*

Schöpf obtained 1:2-naphthocarbazole-3-carboxylic acid by heating dihydro-2-ketonaphthalene-3-carboxylic acid,



(m. p.  $216^{\circ}$ ), with phenylhydrazine, a reaction which would correspond with that described in the present paper, except that the latter acid is already in the ketonic form, and that the addition of phenylhydrazine hydrochloride is unnecessary. Schöpf's synthesis leaves no doubt as to the constitution of 1:2-naphthocarbazole; and, reasoning from the analogy of this compound, we have assigned the 1:2-constitution to all carbazoles obtained by the interaction of

\* Owing to the fact that no reference to Ullmann's work is given in Richter's *Lexikon*, and that only the old inaccurate melting point of the compound appears there, we overlooked Ullmann's correction, and, as stated in our preliminary note on the present synthesis (Proc., 1901, 17, 176), prepared the substance by Schöpf's method in order to compare it with ours. We can confirm Ullmann's statement as to the melting point.

We are indebted to Dr. Ullmann for calling our attention to the foregoing oversight.

It is perhaps fortunate that we were at first unaware of the identity of our compound with that obtained by Schöpf; otherwise we should probably not have troubled to prepare from our substance the various derivatives already described by him. Having done so, however, we are in a position to state that the melting points given by Schöpf for these derivatives are also much too low. In view of these discrepancies we publish our analyses.

2-naphthol with arylhydrazines—an assumption which is further justified by the well-known difficulty of forming 2:3-derivatives of naphthalene.

We prepared and analysed some derivatives of 1:2-naphthocarbazole.

The *picrate* crystallises from benzene in long, slender, ruby-red needles, melting at 174—175° with decomposition.

0.1138 gave 12.4 c.c. moist nitrogen at 13° and 738 mm.  $N = 12.50$ .

$C_{16}H_{11}N, C_6H_2(NO_2)_3 \cdot OH$  requires  $N = 12.55$  per cent.

(This compound is mentioned by Schöpf; but neither melting point nor analysis is given.)

The *nitroso*-derivative was obtained by adding a solution of sodium nitrite in glacial acetic acid to one of 1:2-naphthocarbazole in the same solvent. It is best purified by recrystallisation from light petroleum, from which it is deposited in yellow, flat needles. When rapidly heated, it melts at 144—145° with decomposition. (Schöpf gives 132° as the melting point.)

0.1327 gave 15.6 moist  $N_2 + NO$  at 15.5° and 769 mm. After absorbing  $NO$ , there remained 10.0 c.c. moist nitrogen at 15° and 760 mm.\*  $N = 11.36$ .

$C_{16}H_{10}ON_2$  requires  $N = 11.38$  per cent.

The *acetyl*-derivative was prepared as recommended by Schöpf by boiling 1:2-naphthocarbazole with a mixture of acetic anhydride and sodium acetate. It crystallised from glacial acetic acid in small, pearly laminae melting at 149° (142°, Schöpf).

0.1444 gave 0.4406  $CO_2$  and 0.0704  $H_2O$ .  $C = 83.22$ ;  $H = 5.42$ .

0.2650 „ 12.4 c.c. moist nitrogen at 18° and 758 mm.  $N = 5.39$ .

$C_{18}H_{13}ON$  requires  $C = 83.39$ ;  $H = 5.02$ ;  $N = 5.40$  per cent.

The *benzoyl*-derivative was prepared by boiling 1:2-naphthocarbazole with twice its weight of benzoic anhydride for 1—2 minutes. This gives a better result than the method with benzoic chloride recommended by Schöpf. The substance crystallised from glacial acetic acid in slender needles melting at 189.5° (170°, Schöpf).

0.2894 gave 11.3 c.c. moist nitrogen at 16° and 749 mm.  $N = 4.48$ .

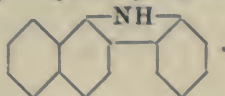
$C_{23}H_{15}ON$  requires  $N = 4.36$  per cent.

Considering that the object of melting-point determinations is to

\* The substance was burnt with copper oxide in a Sprengel vacuum, and there was such a rush of nitric oxide at the beginning of the combustion that much of this gas, as is evident from the above figures, passed undecomposed over the copper spiral.

aid in the identification of chemical substances, it is difficult to see what useful purpose is served by the publication of determinations such as those given by Schöpf, taken, as he mentions, from the *Inauguraldissertation* of one of his pupils.

2 : 1-Naphthocarbazole (*Phenyl- $\alpha$ -naphthylcarbazole*),

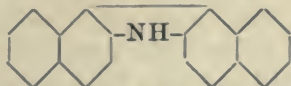


—Ten grams of 1-naphthol, 15 grams of phenylhydrazine, and 8 grams of phenylhydrazine hydrochloride were first heated for a short time at  $165^{\circ}$ , at which temperature the reaction took place, and afterwards at  $180^{\circ}$  for half-an-hour. The product was worked up as in the experiment with 2-naphthol, and the resulting substance was purified by recrystallisation first from benzene and afterwards from light petroleum. It melted at  $225.5^{\circ}$ , and was evidently identical with the 2 : 1-naphthocarbazole (m. p.  $225^{\circ}$ ) obtained by Kym (*Ber.*, 1890, 23, 2465) by desulphurising thiophenyl-1-naphthylamine with finely divided copper. From alcohol it crystallised in leaflets as described by Kym, but from benzene and light petroleum in needles. It had a faint pink tinge, but the smallness of the yield (0.3 gram) precluded further purification. Kym's substance was yellowish. In both cases the colour is doubtless due to impurity.

0.1817 gave 10.4 c.c. moist nitrogen at  $18^{\circ}$  and 755 mm.  $N = 6.56$ .

$C_{16}H_{11}N$  requires  $N = 6.45$  per cent.

s-1 : 2-Dinaphthocarbazole,



— Twenty

grams of 2-naphthol, 26 grams of 2-naphthylhydrazine, and 6 grams of 2-naphthylhydrazine hydrochloride were heated together. The reaction took place about  $140^{\circ}$ , and the mixture was further heated for an hour and a half at  $185$ — $200^{\circ}$ . The melt was worked up as in the previous cases, except that the product which remained after removing basic and phenolic substances was distilled under reduced pressure. The solidified distillate was dissolved in hot benzene, and from the solution the substance was deposited in prisms. These were yellow-coloured; but the colour could be almost entirely removed by recrystallising the compound from light petroleum, from which it separated in needles, or from a mixture of acetone and light petroleum, which deposited it in rhomboidal laminæ: the latter became opaque on drying. The substance melted at  $155^{\circ}$ . On analysis it gave figures agreeing with the formula of s-1 : 2-dinaphthocarbazole.

0.1590 gave 0.5222  $CO_2$  and 0.0759  $H_2O$ .  $C = 89.57$ ;  $H = 5.30$ .

$C_{20}H_{13}N$  requires  $C = 89.88$ ;  $H = 4.87$  per cent.

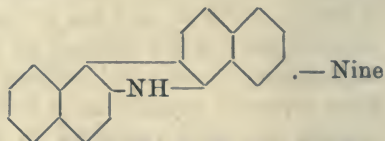


The compound is evidently identical with Walder's *dinaphthylene-amine*, which he obtained by heating 2-dinaphthol with the double compound of zinc chloride and ammonia, and for which he gives the melting point  $157^{\circ}$  (uncorr.) (*Ber.*, 1882, 15, 2173). The substance dissolved in pure concentrated sulphuric acid with a blood-red coloration, as described by Walder. For further identification we prepared the acetyl derivative and the picrate, both of which had the properties mentioned by Walder.

The yield of once-crystallised *s*-1:2-dinaphthocarbazole obtained from the above quantities was 14 grams.

In another preparation of this compound, in which the mother liquors were very carefully worked up, we obtained, in addition, small quantities of 1:2:2':1'-*dinaphthocarbazole* (*v. infra*) and *as*-1:2-dinaphthazine (*m. p.*  $278^{\circ}$ ).

1:2:2':1'-*Dinaphthocarbazole*,



grams of 2-naphthol, 14 grams of 1-naphthylhydrazine, and 3 grams of 1-naphthylhydrazine hydrochloride were heated together. The reaction commenced about  $160^{\circ}$ ; in order to finish it the mixture was kept at  $200^{\circ}$  for an hour. The product was treated as already described. The ethereal solution, freed from basic and phenolic substances, left, on evaporation, a dark residue. By boiling this with benzene, in which it is only sparingly soluble, the carbazole was obtained as an almost white crystalline powder. It dissolves readily in acetone, and on adding light petroleum to the solution, it separates in oblong plates, sometimes with truncated corners and bevelled edges; these crystals contain acetone of crystallisation. Freed from the acetone by heating, the substance melts at  $231^{\circ}$ . It dissolves in a large volume of hot benzene and is deposited in groups of colourless needles with the same melting point. Analysis gave figures agreeing with the formula of 1:2:2':1'-*dinaphthocarbazole*.

0.1491 gave 0.4892  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 89.48$ ;  $\text{H} = 5.21$ .

0.2355 „ 10.8 c.c. moist N at  $17^{\circ}$  and 744 mm.  $\text{N} = 5.21$ .

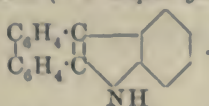
$\text{C}_{20}\text{H}_{13}\text{N}$  requires  $\text{C} = 89.88$ ;  $\text{H} = 4.87$ ;  $\text{N} = 5.24$  per cent.

A determination of acetone in the crystals deposited from a mixture of acetone and light petroleum gave the following result.

0.5507 lost, on heating at  $80^{\circ}$ , 0.0927.  $(\text{CH}_3)_2\text{CO} = 16.83$ .

$\text{C}_{20}\text{H}_{13}\text{N}, (\text{CH}_3)_2\text{CO}$  requires  $(\text{CH}_3)_2\text{CO} = 17.85$  per cent.

## 9 : 10-Phenanthrocarbazole (2'-3'-Diphenyleneindole),

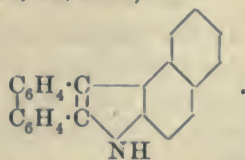


—This compound was, as already mentioned, obtained by Japp and Findlay (*loc. cit.*) by heating a mixture of 9-hydroxyphenanthrene and phenylhydrazine.

We repeated the experiment with the addition of phenylhydrazine hydrochloride to the foregoing mixture, in order to ascertain whether the yield would be thereby improved; but there was practically no difference. The weight of phenanthrocarbazole obtained was very nearly that of the 9-hydroxyphenanthrene taken.

The 9-hydroxyphenanthrene used in this and the following experiments was prepared by boiling phenanthraquinone with hydriodic acid and red phosphorus (compare *Trans.*, 1897, 71, 1118).

## 9 : 10-Phenanthro-1' : 2'-naphthocarbazole,



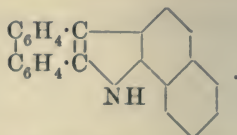
—Five grams of 9-hydroxyphenanthrene, 6 grams of 2-naphthylhydrazine, and 1.5 grams of 2-naphthylhydrazine hydrochloride were heated to 150—160°, at which temperature the chief reaction took place. The mixture was finally heated at 200° for a short time. The product was worked up as in previous cases. The crude carbazole was freed from most of the adhering colouring matter by digesting it with hot benzene, after which it was dissolved in boiling acetone and either benzene or light petroleum added. It separated in rosettes of lustrous, green, flat needles melting at 220°. The green colouring matter could in part be removed by fractional precipitation of the acetone solution with light petroleum; but it re-appeared on recrystallising the substance, which apparently underwent aerial oxidation, yielding the colouring matter.

On analysis it gave figures agreeing with the formula of 9 : 10-phenanthro-1' : 2'-naphthocarbazole. The sample analysed was of a pale green colour.

0.1459 gave 0.4836 CO<sub>2</sub> and 0.0642 H<sub>2</sub>O. C = 90.40; H = 4.88.

0.3216 „ 12.3 c.c. moist nitrogen at 10° and 756 mm. N = 4.55.

C<sub>24</sub>H<sub>15</sub>N requires C = 90.85; H = 4.73; N = 4.41 per cent.

9 : 10-*Phenanthro-2' : 1'-naphthocarbazole*,

—This was prepared as in the case of the preceding compound, using 5 grams of 9-hydroxyphenanthrene, 6 grams of 1-naphthylhydrazine, and 1·5 gram of 1-naphthylhydrazine hydrochloride. The substance was purified in the same way. It crystallised from a mixture of acetone and light petroleum in tufts of slender needles which had a faint brownish tinge and melted constantly at 225·5°. On analysis it gave figures agreeing with the formula of 9 : 10-*phenanthro-2' : 1'-naphthocarbazole*.

0·1565 gave 0·5197 CO<sub>2</sub> and 0·0684 H<sub>2</sub>O. C = 90·57 ; H = 4·85.

0·3312 „ 12·3 c.c. moist nitrogen at 12° and 736 mm. N = 4·27.

C<sub>24</sub>H<sub>15</sub>N requires C = 90·85 ; H = 4·73 ; N = 4·41 per cent.

All the foregoing carbazoles dissolve in concentrated sulphuric acid yielding the coloured solutions characteristic of this group ; but the colorations vary so greatly with the proportion of nitrous acid present in the sulphuric acid that we refrain from describing them.

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UNIVERSITY OF ABERDEEN.

## XXVIII.—*Dimorphism of α-Methylanhydracetonebenzil.*

By FRANCIS R. JAPP, F.R.S., and ARTHUR C. MICHIE, B.Sc.

*α*-METHYLANHYDRACETONEBENZIL,  $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{matrix} > \text{CO}$ , which is best obtained by the action of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol on a mixture of benzil and methyl ethyl ketone at the ordinary temperature, was described by Japp and Meldrum (*Trans.*, 1901, 79, 1029) as forming large, flat crystals, of rhombic outline (“lozenge-shaped”), melting at 118°. These crystals, we find, show oblique extinction in polarised light.

The foregoing form was prepared in this laboratory by three different workers ; and, during three years from the time when it was first obtained, no other form was observed. About a year ago, however, working under apparently the same conditions, we obtained, in place of this compound, a substance melting at 133·5°. It is



deposited from its alcoholic solution in crystals which, when small, are of octahedral habit, but, when large, exhibit more complex forms. These crystals are isotropic in polarised light. They separate much more rapidly from their solutions than the rhombic crystals; and, whereas the latter are obtained in a colourless condition even from coloured solutions, the former are apt to carry down with them a yellow colouring matter. They are, however, colourless when pure. Analysis gave figures agreeing with the formula of a compound formed from benzil and methyl ethyl ketone according to the equation:



0.1583 gave 0.4744  $\text{CO}_2$  and 0.0871  $\text{H}_2\text{O}$ .  $\text{C} = 81.73$ ;  $\text{H} = 6.11$ .

$\text{C}_{18}\text{H}_{16}\text{O}_2$  requires  $\text{C} = 81.82$ ;  $\text{H} = 6.06$  per cent.

From the moment when this substance made its appearance, we never again, except accidentally in one case to be described later on, obtained the rhombic substance melting at  $118^\circ$ , however much we might vary the conditions of experiment.

We at first supposed this octahedral \* compound (m. p.  $133.5^\circ$ ) to be an isomeride of  $\alpha$ -methylanhydracetonebenzil, and accordingly studied its reactions. In every case, however, it yielded the same derivatives as the latter compound; so that, although we had not been able to induce the octahedral compound to crystallise in the rhombic form, we began to suspect that the difference was due merely to dimorphism.

An alcoholic solution of the rhombic form deposited the octahedral form, on sowing it with the latter. This sowing, however, proved to be unnecessary, as the rhombic form was now, by mere recrystallisation, converted into the octahedral form. In order to make sure that the process of boiling with the solvent was not responsible for the transformation, we dissolved some clear rhombic crystals (from former preparations) in cold alcohol, and concentrated the solution in a vacuum over sulphuric acid; but again the octahedral form (m. p.  $133.5^\circ$ ) was deposited.

We next re-determined the melting point of our rhombic specimens, and found, to our surprise, that they only sintered at  $118^\circ$  (their former melting point) and did not really melt until the temperature of  $133.5^\circ$  was reached. On examining the crystals, the reason of this was evident. Some of them were semi-opaque, and were evidently in course of spontaneous transformation into pseudomorphs of the octahedral form; and the older the specimen, the further had this change gone. By selecting clear rhombic crystals for the determination of

\* The terms "octahedral" and "rhombic," which describe roughly the habit of the crystals, are used merely as convenient designations for the two forms.

the melting point, and plunging the capillary tube containing the powdered substance into a bath already heated to 120°, we found that we could fuse the substance; but it instantly resolidified, showing that even these clear crystals contained nuclei of the higher-melting octahedral form. The resolidified substance now melted at 133·5°.

The octahedral form shows no sign of sintering at 118°.

Attempts to obtain the rhombic form by crystallising the octahedral substance at a low temperature yielded only the octahedral form, whether the crystallisation was allowed to take place in open vessels or in hermetically sealed tubes. The use of sealed tubes at the ordinary temperature gave the same result.

In one experiment, however, in which an impure specimen of the rhombic substance, which had been prepared about three years previously and of which the crystals had become in part semi-opaque, was dissolved in hot alcohol and allowed to stand in a covered beaker, the solution was found to have deposited (1) an aggregate of yellow octahedral crystals and (2) a single colourless rhombic crystal of considerable size. This rhombic substance only sintered when slowly heated to 118°, but could be made to fuse at that temperature by plunging it into the already heated bath. The mother liquor from the above crystals deposited, by spontaneous evaporation, *only the octahedral form*.

The foregoing experiment is a further indication that the difference of the two forms is due merely to dimorphism. Since the rhombic form is considerably the more soluble, it is evident that, if the two forms were chemically distinct, there ought—unless the case is one of tautomeric change, which seems to us improbable—to have been a preponderating amount of the rhombic substance left in the mother liquor. But there was none.

The authors wish to call attention to this case of dimorphism, as other investigators, who might happen to obtain the more stable form first, would probably fail to recognise the substance as chemically identical with that described by Japp and Meldrum.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF ABERDEEN.

XXIX.—*The Oxidation Products of the Methyl Homologues of Anhydracetonebenzil.*

By FRANCIS R. JAPP, F.R.S., and ARTHUR C. MICHIE, B.Sc.

THE oxidation of anhydracetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$ , was studied by Japp and Lauder (Trans., 1897, 71, 132). By oxidising it with sodium hypobromite, they obtained desyleneacetic acid,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$ ; whilst chromium trioxide, in acetic acid solution, was found to convert it into  $\alpha\beta$ -diphenyl- $\alpha\beta$ -dihydroxyglutaric acid,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ .

We have now studied the oxidation of  $\alpha$ -methylanhydracetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$  (m. p. 118° and 133·5°);  $\beta$ -methylanhydracetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}$  (m. p. 180°);  $\alpha\beta$ -dimethylanhydracetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}$  (m. p. 150°); and  $\beta\beta$ -dimethylanhydracetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 \end{array} > \text{CO}$  (m. p. 181°). (Compare the preceding paper; also Japp and Meldrum, Trans., 1901, 79, 1028.) The remaining methyl homologue,  $\alpha\beta\beta$ -trimethylanhydracetonebenzil, owing to the difficulty of obtaining it in quantity, was not included in the investigation.

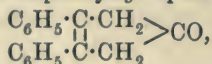
Of the foregoing homologues, only  $\alpha$ -methylanhydracetonebenzil is attacked by potassium hypobromite. It yields  $\alpha$ -desylenepropionic acid (m. p. 174·5°):



together with *diphenylmaleic acid*; the latter, when liberated from its salt, is converted into its anhydride. From its formation from a closed-chain compound of the above formula,  $\alpha$ -desylenepropionic acid must have the configuration,  $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \end{array}$ . The reaction is analogous to that in which anhydracetonebenzil is oxidised by hypobromite to desyleneacetic acid, but in the latter case no formation of diphenylmaleic acid was observed. The formation of diphenylmaleic acid involves a shifting of the double bonds in  $\alpha$ -methylanhydracetone-

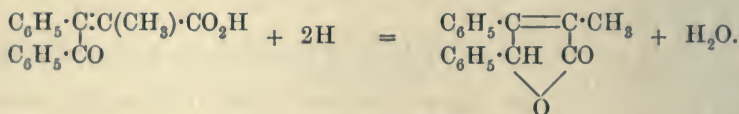


benzil, so as to form the group  $C_6H_5 \cdot \overset{|}{\underset{|}{C}} \cdot \overset{|}{\underset{|}{C}} \cdot C_6H_5$ , the change being accompanied by a migration of the hydroxyl group. This change in the position of the double bonds in the *cyclopentene* ring is of frequent occurrence in the reactions of anhydracetonebenzil and its derivatives: thus, in the formation of diphenyl*cyclopentenone*,



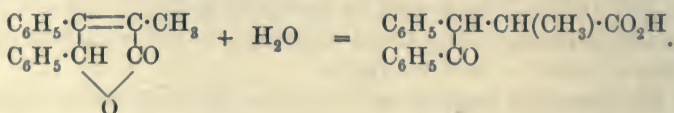
and its homologues. The formation of diphenylmaleic acid (along with diphenylfumaric acid) from a compound belonging to this group, has already been observed in the oxidation of anhydracetonebenzil-carboxylic acid with alkaline hypobromite (Japp and Lander, *Trans.*, 1897, 71, 142).

Boiling with hydriodic acid converts  $\alpha$ -desylenepropionic acid into 1-methyl-2 : 3-diphenyl- $\Delta^1$ -crotolactone\* (m. p. 88.5°):



This reaction exactly corresponds with the formation of the stable diphenylcrotolactone melting at 151.5° (according to Thiele, the  $\Delta^1$ -crotolactone) by the action of hydriodic acid on desyleneacetic acid, except that in the latter case a portion of the diphenylcrotolactone is hydrolysed to desylacetic acid (Japp and Lander, *Trans.*, 1897, 71, 156).

By warming methyl diphenylcrotolactone with alcoholic potassium hydroxide it is converted into Knoevenagel's  $\alpha$ -desylpropionic acid:

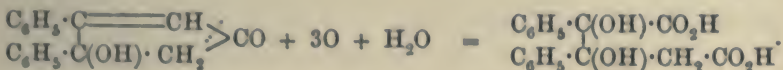


On the other hand, when  $\alpha$ -desylpropionic acid is distilled under reduced pressure it parts with water and is reconverted into *methyl-diphenylcrotolactone*.

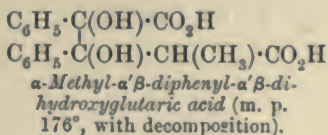
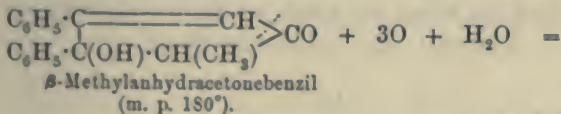
In the oxidation of anhydracetonebenzil with chromium trioxide, studied by Japp and Lander (*Trans.*, 1897, 71, 133), the closed chain opens at the point between the carbonyl and the ethylene group, and the latter group is hydroxylated, whilst at the same time its end carbon atom and the carbonyl group are oxidised to carboxyl

\* The reasons for adopting the  $\Delta^1$ -unsaturated constitution for this stable lactone of  $\alpha$ -desylpropionic acid, instead of the apparently more obvious  $\Delta^2$ -unsaturated constitution, reserving the latter for the isomeric labile lactone (not yet prepared), are to be found in Thiele's paper: "Ueber isomere Diphenylcrotolactone" (*Annalen*, 1899, 306, 194).

groups, a dibasic acid resulting— $\alpha\beta$ -diphenyl- $\alpha\beta$ -dihydroxyglutaric acid :



We find that the oxidation of  $\beta$ -methylanhydracetonebenzil with chromium trioxide proceeds on strictly analogous lines :

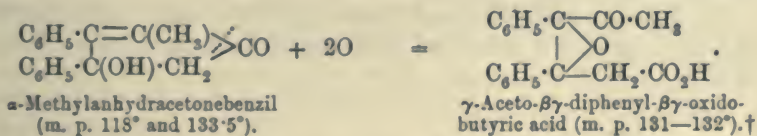


In the case of the other methyl homologues of anhydracetonebenzil which we have examined, oxidation with chromium trioxide opens the closed chain in the same place ; but the further course of the reaction is governed both by the position and by the number of the methyl groups. Thus :

1. The presence of a methyl group in the  $\alpha$ -position (i.e., in the CH-group) of anhydracetonebenzil prevents the formation of a dibasic acid, and a ketonic acid is formed instead.

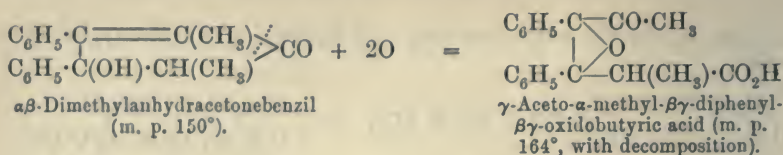
2. The presence of a methyl group in the  $\alpha$ -position, or of two methyl groups in the  $\beta$ -position (i.e., in the  $\text{CH}_2$ -group), leads to the elimination of water from the resulting acid, so that the group  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{C} \end{array} \text{O}$ , is formed.\*

The following oxidations with chromium trioxide illustrate these rules :



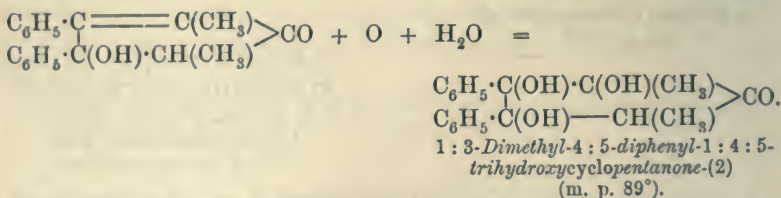
\* The action of alkyl groups in promoting the elimination of water—as, for example, in the case of homologues of maleic acid—is too familiar to call for remark.

† There is, so far as we are aware, no convenient nomenclature for “bridge-oxygen”—oxygen uniting two carbon atoms which are already either directly or indirectly united. We would suggest the prefix “oxido” as supplying this want. Thus glycidic acid would be “ $\alpha\beta$ -oxidopropionic acid,” the bridge-oxygen being thus regarded as a bivalent substituent. This prefix has the analogy of “imido” to recommend it.

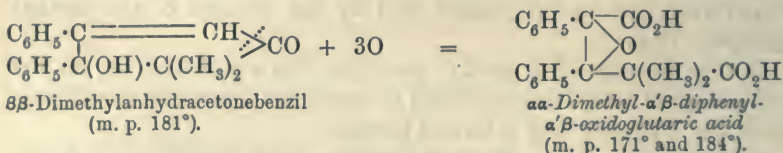


The two foregoing oxidations illustrate Rules 1 and 2.

In oxidising  $\alpha\beta$ -dimethylanhydracetonebenzil with chromium trioxide, another portion of the substance yields a neutral compound, in the formation of which the closed chain is not opened :



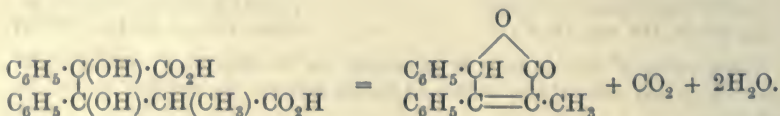
The oxidation of  $\beta\beta$ -dimethylanhydracetonebenzil, on the other hand, illustrates Rule 2 :



Here the oxidation follows the same course as in the cases of anhydracetonebenzil and  $\beta$ -methylanhydracetonebenzil, except that, under the influence of the two methyl groups, the resulting compound parts with water, passing into the oxido-form.

In the present introduction we will describe only those reactions of the foregoing oxidation products which admit of a theoretical interpretation.

By boiling methyldiphenyldihydroxyglutaric acid with fuming hydriodic acid it is converted into *methyldiphenylcrotonolactone* (m. p.  $88.5^\circ$ ):

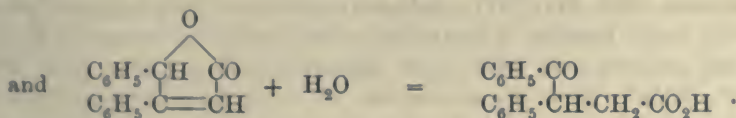
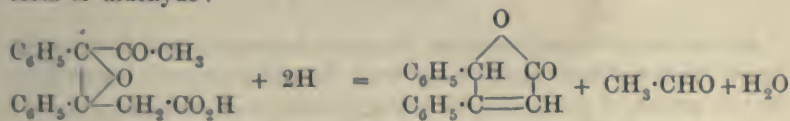


and as there is no reduction involved, hydrochloric acid effects the same transformation, although only very imperfectly. The reaction corresponds with that in which diphenyldihydroxyglutaric acid is converted, under the influence of hydracids, into a mixture of diphenyl-

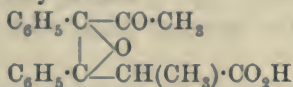


$\Delta^1$ -crotonolactone (m. p.  $151.5^\circ$ ) and desylacetic acid (Japp and Lander, Trans., 1897, 71, 127).\*

When acetodiphenyloxidobutyric acid is boiled with fuming hydriodic acid, it yields a mixture of *diphenyl- $\Delta^1$ -crotonolactone* (m. p.  $151.5^\circ$ ) and *desylacetic acid*, the aceto-group being eliminated, possibly in the form of aldehyde :



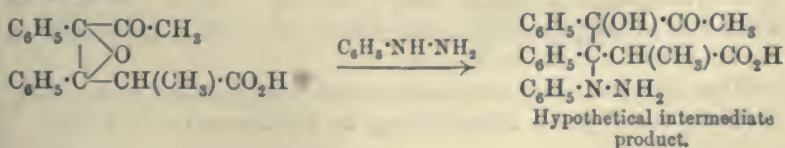
Acetodiphenyloxidobutyric acid forms a *semicarbazone*. It also interacts with phenylhydrazine; but we were unable to purify the resulting compound, a failure which is to be regretted, as the reactions of the other oxido-acids—acetomethyldiphenyloxidobutyric acid and dimethyldiphenyloxidoglutaric acid—with phenylhydrazine are quite abnormal, the oxido-group taking part in the reaction. Thus acetomethyldiphenyloxidobutyric acid



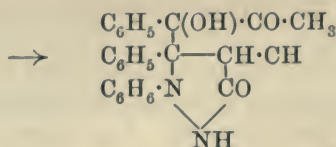
interacts with phenylhydrazine according to the equation :



yielding a *neutral compound* melting at  $212^\circ$ . As the acid thus interacts with phenylhydrazine with elimination of only 1 mol. of water, forming a compound which is no longer an acid, it is clear that the carbonyl of the aceto-group does not take part in the reaction, as the joint action of the carbonyl and carboxyl groups on a mol. of phenylhydrazine would involve the elimination of 2 mols. of water, not to mention the fact that the carbonyl group is in the  $\delta$ -position to the carboxyl group, a circumstance which would render such joint action impossible. The following scheme would furnish an explanation of the reaction :



\* The diphenylcrotonolactone is there represented, according to the view at that time prevailing as the  $\Delta^2$ -unsaturated compound.



Compound, m. p. 212°.

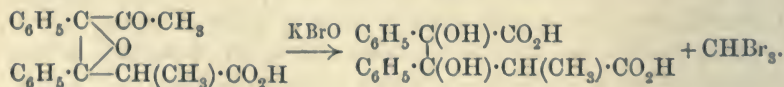
According to this explanation the basic imino-group of the phenylhydrazine first interacts additively with the oxido-group of the acid, as in the action of piperidine on phenylglycidic acid (Erlenmeyer, jun., *Annalen*, 1892, 271, 157); and then this intermediate compound parts with water forming a pyrazolidone ring, as in the interaction of the  $\beta$ -halogen-propionic acids with phenylhydrazine (*Ber.*, 1891, 24, Ref., 234).<sup>\*</sup> That the elimination of water from the hypothetical intermediate compound does not occur between carboxyl and hydroxyl so as to form a lactone is shown by the fact that the resulting compound does not yield a salt with alcoholic potash.

The corresponding abnormal reaction of dimethyldiphenyloxido-glutaric acid will be described further on.

Acetomethyldiphenyloxidobutyric acid yields an oxime in which the carbonyl of the aceto-group is oximated, the reaction, unlike that with phenylhydrazine just described, being perfectly normal. The oxime contains the carboxyl group and dissolves in sodium carbonate.

When heated, acetomethyldiphenyloxidobutyric acid parts with carbon dioxide, yielding  $\beta$ -aceto- $\alpha$ -ethyl- $\alpha\beta$ -diphenyloxidoethane,  $\text{C}_6\text{H}_5 \cdot \text{C} - \text{CO} \cdot \text{CH}_3$  (m. p. 98—99°). This yields a semicarbazone,  $\text{C}_6\text{H}_5 \cdot \text{C} - \text{C}_2\text{H}_5$  (m. p. 204°).  $\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}_3$

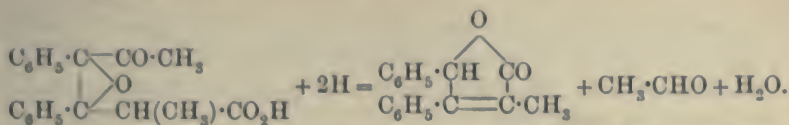
Potassium hypobromite oxidises acetomethyldiphenyloxidobutyric acid to  $\alpha$ -methyl- $\alpha'\beta$ -diphenyl- $\alpha'\beta$ -dihydroxyglutaric acid:



The product is identical with the acid obtained by the oxidation of  $\beta$ -methylanhydracetonebenzil with chromium trioxide. It is to be noted how, in the present case, the removal of a methyl group leads to the re-hydration of the oxido-group.

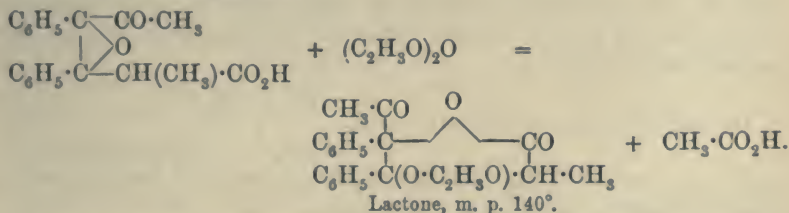
When acetomethyldiphenyloxidobutyric acid is boiled with fuming hydriodic acid it yields methylldiphenyl- $\Delta^1$ -crotolactone (m. p. 88.5°):

<sup>\*</sup> One of us is at present engaged, conjointly with Mr. W. Maitland, in studying the action of phenylhydrazine on sodium phenylglycidate, and the results obtained, which we hope to publish shortly, entirely confirm the above interpretation.

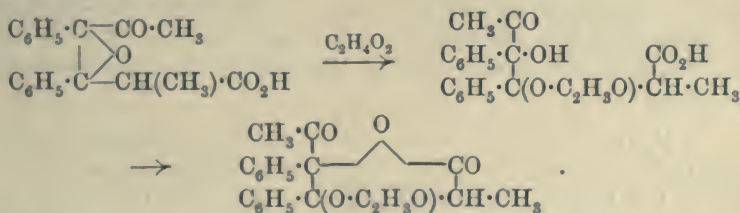


This change corresponds with that which acetodiphenyloxidobutyric acid undergoes under the same conditions (*v. supra*), except that in the present case, owing to the dehydrating action of the methyl group, only the unsaturated lactone, and none of the corresponding ketonic acid, is formed.

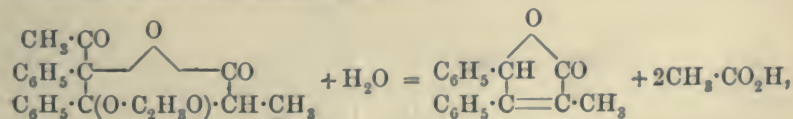
By the action of acetic anhydride, mixed with a few drops of concentrated sulphuric acid, on acetomethyldiphenyloxidobutyric acid in the cold, a *lactone* of the formula  $\text{C}_{21}\text{H}_{20}\text{O}_5$  (m. p.  $140^\circ$ ) is formed according to the equation :



The foregoing process might be regarded as an addition of  $\text{CH}_3 \cdot \text{CO}_2$  and H to the oxido-group, the resulting compound then parting with water to form a lactone :



When this lactone is treated with alcoholic potassium hydroxide it yields *α-desylpropionic acid*. Possibly methyldiphenyl- $\Delta^1$ -crotonolactone is formed as an intermediate product :

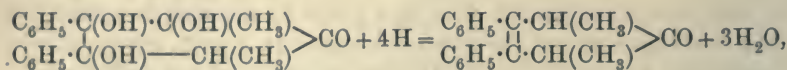


the lactone being then hydrolysed to *α-desylpropionic acid* as already described.

The neutral compound obtained along with acetomethyldiphenyloxidobutyric acid by the oxidation of  $\alpha\beta$ -dimethylanhydracetonebenzil, is, as already stated, to be regarded as a dimethyldiphenyltrihydroxy-



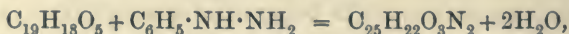
cyclopentanone. That the pentacarbon ring is still intact in this compound is shown by the fact that, by boiling the substance with hydriodic acid, it yields, along with other products, *dimethyldiphenylcyclopentenone* (m. p. 122°):



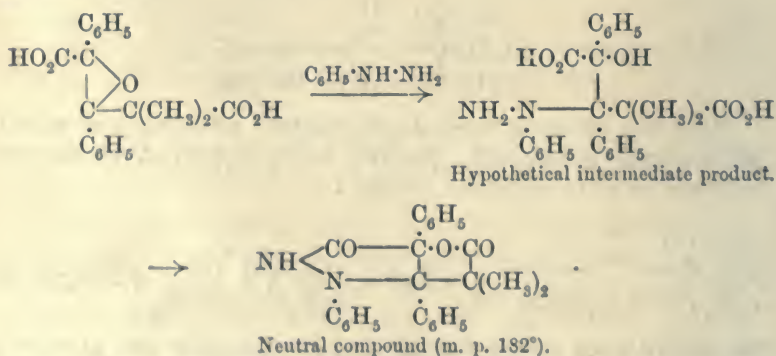
a compound which can also be obtained by the reduction of  $\alpha\beta$ -dimethylanhydracetonebenzil. The latter reaction will be described in a subsequent communication, where the reasons for assigning to the compound the foregoing constitution will also be given.

Dimethyldiphenyltrihydroxycyclopentanone forms a *semicarbazone*,  $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_3$ . It also yields a number of other transformation products; but, as the constitution of most of these admits of more than one interpretation, we will confine ourselves to describing later on the experimental results.

Dimethyldiphenyloxidoglutaric acid,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \dot{\text{C}} - \text{CO}_2\text{H} \\ | \quad \diagup \text{O} \\ \text{C}_6\text{H}_5 \cdot \dot{\text{C}} - \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2\text{H} \end{array}$ , the oxidation product of  $\beta\beta$ -dimethylanhydracetonebenzil, interacts with phenylhydrazine according to the equation:



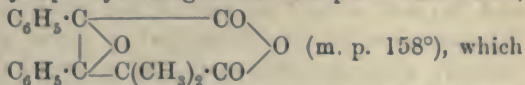
yielding a *neutral* compound melting at 182°. The reaction resembles that of acetomethyldiphenyloxidobutyric acid already described, and in both cases the oxido-group takes part in the reaction. The mechanism of the process may, in the present case, be represented as follows:



As in the former case, so here also the first stage of the process may be assumed to be an additive interaction between the phenylhydrazine and the oxido-group of the acid; but in the present reaction the resulting intermediate compound parts with *two* mols. of water, yield-

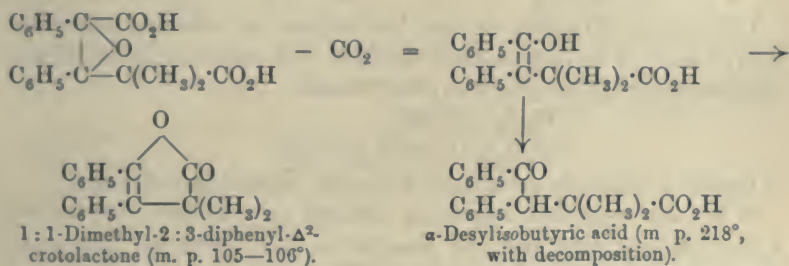
ing a substance which contains both the lactone ring and the pyrazolidone ring. Its lactonic character is shown by the fact that it yields a salt with potassium hydroxide, and that the resulting acid, when freshly precipitated, dissolves in alkaline carbonates, but, on drying, or on recrystallisation, is reconverted into the neutral compound melting at  $182^{\circ}$ .

When heated, dimethyldiphenyloxidoglutaric acid parts with water, yielding the *anhydride*



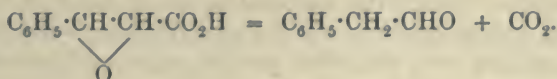
may also be obtained by the action of acetic anhydride, with the addition of a few drops of concentrated sulphuric acid, on the acid in the cold. Treated with alkalis the anhydride regenerates the acid.

By boiling with dilute sulphuric acid, dimethyldiphenyloxidoglutaric acid is converted, partly into the foregoing anhydride, and partly, with elimination of carbon dioxide and water, into 1:1-dimethyl-2:3-diphenyl- $\Delta^2$ -crotolactone, a little  $\alpha$ -desylisobutyric acid being formed at the same time:



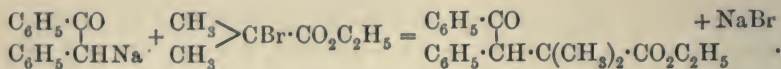
In this case, only the  $\Delta^2$ -crotolactone can be formed, as there is no hydrogen attached to the  $\alpha$ -carbon atom of  $\alpha$ -desylisobutyric acid.

The formation of  $\alpha$ -desylisobutyric acid from dimethyldiphenyloxidoglutaric acid is analogous to that of phenylacetaldehyde from phenylglycidic acid:



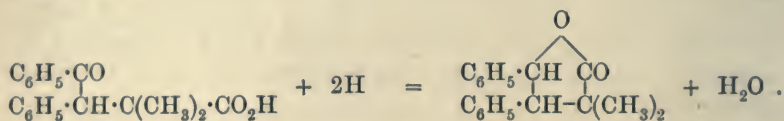
The formation of desylacetic acid from acetodiphenyloxidobutyric acid, and of  $\alpha$ -desylpropionic acid (or rather of its lactone—methyl-diphenyl- $\Delta^1$ -crotolactone) from acetomethyldiphenyloxidobutyric acid (*v. supra*), belong to the same category, except that in the two latter cases, the aceto-group is eliminated in place of carbon dioxide.

The constitution of  $\alpha$ -desylisobutyric acid was proved by synthesising it from sodium deoxybenzoin and ethyl  $\alpha$ -bromisobutyrate, hydrolysing, with caustic alkali, the ester thus obtained:

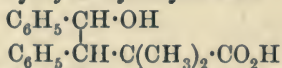


By the action of acetic anhydride, containing a little concentrated sulphuric acid, on *α*-desylisobutyric acid in the cold, the foregoing *dimethyldiphenylcrotonolactone* (m. p. 105—106°) is formed.

When dimethyldiphenyloxidoglutaric acid is boiled with hydriodic acid, it yields, as first product of the reaction, *α*-desylisobutyric acid, the reaction so far resembling that of dilute sulphuric acid just described; but a reduction compound is formed at the same time, and if the boiling is continued sufficiently long, the *α*-desylisobutyric acid is converted into this reduction compound, which is the dimorphous *lactone* (m. p. 106° and 110°) of *αα*-dimethyl-*βγ*-diphenyl-*γ*-hydroxybutyric acid



This saturated lactone can also be obtained by reducing *α*-desylisobutyric acid in boiling alcoholic solution with sodium. A salt of the above dimethyldiphenylhydroxybutyric acid

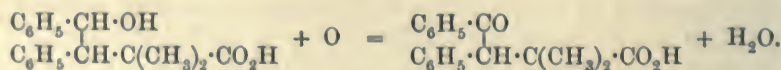


is formed; the latter acid, when liberated, yields the lactone.

When the saturated lactone is reduced at a higher temperature with hydriodic acid and red phosphorus, it is converted into *αα*-dimethyl-*βγ*-diphenylbutyric acid (m. p. 172°):

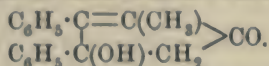


On the other hand, if the saturated lactone is dissolved in potassium hydroxide, and the resulting salt of dimethyldiphenyl-*γ*-hydroxybutyric acid is oxidised with potassium permanganate, *α*-desylisobutyric acid is obtained:





## EXPERIMENTAL.

I.  $\alpha$ -METHYLANHYDRACETONEBENZIL,A. Oxidation of  $\alpha$ -Methylanhydracetonebenzil with Potassium Hypobromite.

Five grams of finely-powdered  $\alpha$ -methylanhydracetonebenzil were suspended in an alkaline solution of potassium hypobromite (prepared by adding 15 grams of bromine to a solution of 30 grams of potassium hydroxide in 300 c.c. of water), and the mixture was stirred for 24 hours by means of a mechanical stirrer. The unchanged substance was removed by filtration, and the filtrate, after addition of sulphurous acid, was acidified with hydrochloric acid. The pale yellow precipitate was dissolved in ether, and the ethereal solution was extracted first with sodium carbonate solution, and afterwards with a solution of sodium hydroxide. The acid obtained on acidifying the sodium carbonate extract was crystallised from a mixture of benzene and light petroleum ("ligroin"). It formed groups of slender needles melting constantly at  $174.5^\circ$ , and on analysis gave figures agreeing with the formula of  $\alpha$ -desylenepropionic acid,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{C}(\text{CH}_3) \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$ .

0.1560 gave 0.4387  $\text{CO}_2$  and 0.0769  $\text{H}_2\text{O}$ .  $\text{C} = 76.69$ ;  $\text{H} = 5.47$ .

$\text{C}_{17}\text{H}_{14}\text{O}_3$  requires  $\text{C} = 76.69$ ;  $\text{H} = 5.26$  per cent.

The acid did not dissolve readily in dilute ammonia, and an attempt to prepare the silver salt from the ammonium salt by precipitation did not yield a pure product.

The sodium hydroxide extract above referred to yielded, on acidifying, a yellow precipitate which, on recrystallisation from benzene, was obtained in thick yellow needles showing a green fluorescence and melting at  $156^\circ$ . These are the properties of diphenylmaleic anhydride,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O}$ , and, on mixing the substance with a sample of the latter compound, the melting point was not depressed.

0.1519 gave 0.4280  $\text{CO}_2$  and 0.0595  $\text{H}_2\text{O}$ .  $\text{C} = 76.84$ ;  $\text{H} = 4.35$ .

$\text{C}_{16}\text{H}_{10}\text{O}_3$  requires  $\text{C} = 76.80$ ;  $\text{H} = 4.00$  per cent.

Oxidation of 5 grams of  $\alpha$ -methylanhydracetonebenzil yielded 0.4 gram of  $\alpha$ -desylenepropionic acid and 1.6 gram of diphenylmaleic anhydride, whilst two grams of the original substance were recovered unchanged.

*Reduction of  $\alpha$ -Desylenepropionic Acid; Formation of 1-Methyl-2:3-di-*

*phenyl-Δ<sup>1</sup>-crotonolactone*, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C} \cdot \text{CH}_3 \\ | \quad \quad | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \quad \text{CO} \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{O} \end{array}$$
—One gram of the acid was

boiled with fuming hydriodic acid (sp. gr. 1.96) for 5 minutes. The product was dissolved in ether and treated with solutions of sulphurous acid and sodium carbonate. The residue obtained on evaporation of the ether was crystallised from methyl alcohol. Tabular crystals were deposited melting at 70—71°; but after standing for some weeks they turned opaque and then melted at 88.5°. The latter is the melting point of *methyldiphenylcrotonolactone*—a substance obtained in various other reactions in the course of this work. The present specimen was further identified by the mixture melting-point method, a sample of the compound prepared from acetomethyldiphenyloxido-butyric acid (*v. infra*) being employed for comparison.

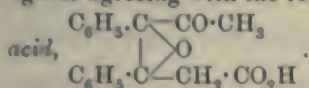
The lower melting point of 70—71° was not observed except in the case of the foregoing preparation.

#### B. Oxidation of *α*-Methylanhydracetonebenzil with Chromium Trioxide.

To a solution of 10 grams of *α*-methylanhydracetonebenzil \* in glacial acetic acid, a solution of 15 grams of chromium trioxide in the same menstruum was very gradually added, the mixture being cooled with water and stirred during the process. The whole was allowed to stand in the cold for 3 days, after which it was poured into excess of water. The dark green, viscid precipitate was separated and extracted with ether, and the ethereal solution was shaken with aqueous sodium carbonate. On acidifying the alkaline solution an organic acid was precipitated as a pale green oil which afterwards solidified. This was redissolved in ether, the solution was re-extracted with sodium carbonate, and the alkaline solution was *gently* warmed for some time; this caused the separation of chromium compounds, which were removed by filtration. On acidifying, the acid, now free from chromium, was precipitated. (If the alkaline solution is too strongly heated in the foregoing process the acid obtained is yellow.) It crystallises from dilute alcohol, or from a mixture of ether and light petroleum, in slender needles melting at 131—132° with decomposition. On several occasions it was noticed that on allowing the needles to stand in contact with the dilute alcoholic mother liquor, they were transformed into tabular crystals with the same melting point; these could be converted into needles by recrystallisation from the mixture of ether and light petroleum.

\* In the earlier experiments the modification of *α*-methylanhydracetonebenzil melting at 118° was employed; in the later, that melting at 133.5°. (See preceding paper.) Both yielded the same product. The same applies to the hypobromite oxidation just described.

Analyses, in which different preparations were employed, gave figures agreeing with the formula of  $\gamma$ -aceto- $\beta\gamma$ -diphenyl- $\beta\gamma$ -oxidobutyric acid,



0.1893 gave 0.5033  $\text{CO}_2$  and 0.0938  $\text{H}_2\text{O}$ . C = 72.51; H = 5.50.

0.1519 " 0.4073  $\text{CO}_2$  " 0.0752  $\text{H}_2\text{O}$ . C = 73.13; H = 5.50.

0.1966 " 0.5249  $\text{CO}_2$  " 0.0968  $\text{H}_2\text{O}$ . C = 72.81; H = 5.47.

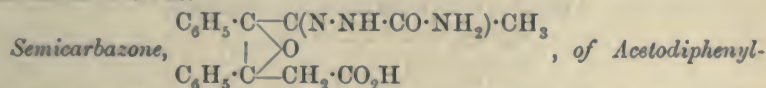
$\text{C}_{18}\text{H}_{16}\text{O}_4$  requires C = 72.97; H = 5.40 per cent.

The silver salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt:

0.4169 gave 0.1109 Ag. Ag = 26.60.

$\text{C}_{18}\text{H}_{15}\text{O}_4\text{Ag}$  requires Ag = 26.78 per cent.

The yield of pure acid from 10 grams of  $\alpha$ -methylanhydracetonebenzil was only 0.5 gram. Owing to the difficulty of obtaining the acid in quantity we have been unable to study it with the requisite thoroughness, and the constitution which we assign to it is based chiefly on its analogy to its homologue acetomethyldiphenyloxidobutyric acid, the product of the oxidation of  $\alpha\beta$ -dimethylanhydracetonebenzil with chromium trioxide.



*oxidobutyric Acid*.—0.7 gram of semicarbazide hydrochloride was dissolved in a very little warm water and mixed with an alcoholic solution of 0.6 gram of potassium acetate. After filtering off the potassium chloride, the filtrate was added to an alcoholic solution of 0.6 gram of the foregoing acid, and the mixture was allowed to stand. After two days the crystals which had formed were separated and recrystallised from alcohol, from which they were deposited in groups of small needles melting at  $198^\circ$  with decomposition. The compound was soluble in sodium carbonate, showing that the carboxyl group had not taken part in the reaction.

A nitrogen determination gave figures which were somewhat lower than those required by the *semicarbazone*; but we had no acid to spare for a second preparation.

0.1368 gave 13.6 c.c. moist nitrogen at  $21^\circ$  and 760 mm. N = 11.32.

$\text{C}_{19}\text{H}_{19}\text{O}_4\text{N}_3$  requires N = 11.89 per cent.

*Action of Hydriodic Acid on Acetodiphenyloxidobutyric Acid: Formation of Desylacetic Acid,*

$$\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \end{array} \quad \text{and Diphenyl-}\Delta^1\text{-croto-}$$



$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{CH} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \end{array}$$
 —Acetodiphenyloxidobutyric acid was boiled with excess of fuming hydriodic acid for 2 minutes. The product was dissolved in ether and treated with sulphurous acid; sodium carbonate then removed an organic acid, whilst a neutral substance remained in the ether. The acid crystallised from alcohol in the lustrous octahedra of *desylacetic acid*, melting at  $161^\circ$ ; and its melting point was not altered by mixing it with a specimen of *desylacetic acid*.

0.1532 gave 0.4254  $\text{CO}_2$  and 0.0774  $\text{H}_2\text{O}$ .  $\text{C} = 75.72$ ;  $\text{H} = 5.61$ .

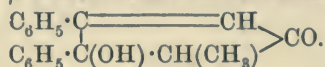
$\text{C}_{16}\text{H}_{14}\text{O}_3$  requires  $\text{C} = 75.59$ ;  $\text{H} = 5.51$  per cent.

The neutral substance which remained after removing the *desylacetic acid* was recrystallised from a mixture of benzene and light petroleum. It was deposited in prismatic needles melting at  $151.5^\circ$ , and proved to be *diphenyl- $\Delta^1$ -crotonolactone*. This was confirmed by the mixture melting-point test:

0.1591 gave 0.4768  $\text{CO}_2$  and 0.0739  $\text{H}_2\text{O}$ .  $\text{C} = 81.73$ ;  $\text{H} = 5.16$ .

$\text{C}_{16}\text{H}_{12}\text{O}_2$  requires  $\text{C} = 81.35$ ;  $\text{H} = 5.09$  per cent.

## II. $\beta$ -METHYLANHYDRACETONEBENZIL,



### *Oxidation of $\beta$ -Methylanhydracetonebenzil with Chromium Trioxide.*

Ten grams of  $\beta$ -methylanhydracetonebenzil (m. p.  $180^\circ$ ) in fine powder were suspended in 40 c.c. of glacial acetic acid, and a solution of 15 grams of chromium trioxide in the same solvent was added fairly rapidly, using a mechanical stirrer and cooling during the process. During the addition of the chromium trioxide the suspended substance went into solution. After standing in the cold for three days, the mixture was diluted with water, and the green precipitate was filtered off and dissolved in sodium carbonate. The alkaline solution was digested for several hours on the water bath, after which it was filtered from chromium compounds and acidified. If the acid precipitated is not quite colourless, it should be redissolved in sodium carbonate and the warming continued. A further quantity of the acid may be obtained from the original dilute acetic acid filtrate by extraction with ether. The acid was crystallised from ether, from which it separates in obliquely-terminated four-sided prisms melting at  $176^\circ$  with decomposition. In polarised light the crystals show an extinction angle of  $22^\circ$ . It is readily soluble in alcohol, acetone, and ethyl acetate, very sparingly soluble in benzene. The yield is fair,

5—6 grams of the acid being obtained from 10 grams of  $\beta$ -methyl-anhydracetonebenzil.

Analysis gave figures agreeing with the formula of  $\alpha$ -methyl- $\alpha'$ -diphenyl- $\alpha'$ - $\beta$ -dihydroxyglutaric acid,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H} \end{array}$$

0.1267 gave 0.3037  $\text{CO}_2$  and 0.0632  $\text{H}_2\text{O}$ .  $\text{C} = 65.36$ ;  $\text{H} = 5.54$ .

0.1369 „ 0.3274  $\text{CO}_2$  and 0.0698  $\text{H}_2\text{O}$ .  $\text{C} = 65.22$ ;  $\text{H} = 5.66$ .

$\text{C}_{18}\text{H}_{18}\text{O}_6$  requires  $\text{C} = 65.45$ ;  $\text{H} = 5.45$  per cent.

The silver salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt.

0.2074 gave 0.3045  $\text{CO}_2$ , 0.0535  $\text{H}_2\text{O}$  and 0.0829 Ag.  $\text{C} = 40.04$ ;  $\text{H} = 2.86$ ;  $\text{Ag} = 39.97$ .

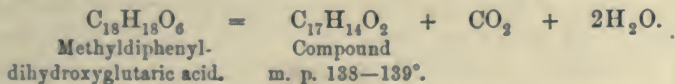
$\text{C}_{18}\text{H}_{16}\text{O}_6\text{Ag}_2$  requires  $\text{C} = 39.71$ ;  $\text{H} = 2.94$ ;  $\text{Ag} = 39.69$  per cent.

*Action of Heat on Methylphenyldihydroxyglutaric Acid.*—A quantity of the acid was distilled under reduced pressure. The distillate, which was a pale-yellow, viscid substance, was treated with ether, which deposited it in large tabular crystals, of rhombic outline. Recrystallised from alcohol, they melted constantly at  $138$ — $139^\circ$ . Analysis gave figures agreeing with the formula  $\text{C}_{17}\text{H}_{14}\text{O}_2$ .

0.1551 gave 0.4631  $\text{CO}_2$  and 0.0817  $\text{H}_2\text{O}$ .  $\text{C} = 81.43$ ;  $\text{H} = 5.85$ .

$\text{C}_{17}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 81.60$ ;  $\text{H} = 5.60$  per cent.

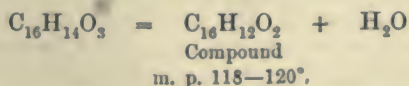
By heating the acid, first at  $155^\circ$  and afterwards at  $215^\circ$ , in a Sprengel vacuum and pumping off and measuring the gas, it was found that exactly 1 mol. of carbon dioxide was eliminated. Water was also seen to be given off. The compound is formed according to the equation,



Japp and Lander showed that diphenyldihydroxyglutaric acid, when heated at  $105^\circ$ , yielded isocinnamylmandelic acid according to the equation,



and that, when the isocinnamylmandelic acid thus formed was heated at  $160^\circ$ , it decomposed as follows:



(Trans., 1897, 71, 134 and 139). The foregoing compound  $\text{C}_{17}\text{H}_{14}\text{O}_2$  is doubtless the methyl homologue of this  $\text{C}_{16}\text{H}_{12}\text{O}_2$ , and the reaction

in which it is formed is a combination of the two just quoted. An attempt which we made to stop this reaction half way, so as to obtain a methyl homologue of isocinnamonylmandelic acid, led to no result.

*Action of Hydriodic Acid on Methylldiphenyldihydroxyglutaric Acid:*

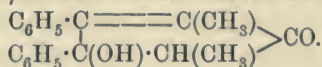
*Formation of Methylldiphenyl- $\Delta^1$ -crotonolactone,* 
$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{CH} \quad \text{CO} \\ | \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{C} = \text{C} \cdot \text{CH}_3 \end{array} \text{—The}$$
 acid was boiled for two minutes with fuming hydriodic acid, and the product was purified in the usual way. The compound was deposited from ether in transparent, thick crystals of rhombic outline, melting at  $88.5^\circ$ , and proved to be *methylldiphenylcrotonolactone*. It was further identified by the mixture melting-point test, and this result was confirmed by analysis.

0.1630 gave 0.4866  $\text{CO}_2$  and 0.0839  $\text{H}_2\text{O}$ .  $\text{C} = 81.41$ ;  $\text{H} = 5.71$ .

$\text{C}_{17}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 81.60$ ;  $\text{H} = 5.60$  per cent.

As the process in which the foregoing compound is formed is not a reduction, we tried whether fuming hydrochloric acid would effect the same change as hydriodic acid. Methylldiphenyldihydroxyglutaric acid was therefore boiled with fuming hydrochloric acid for ten minutes; but only about 10 per cent. of it was transformed into methylldiphenylcrotonolactone, the remainder being recovered unchanged.

### III. $\alpha\beta$ -DIMETHYLANHYDRACETONEBENZIL,



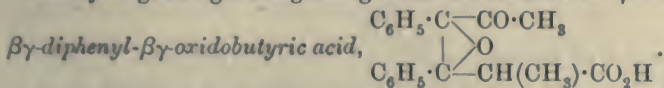
*Oxidation of  $\alpha\beta$ -Dimethylanhydracetonebenzil with Chromium Trioxide.*

Twenty grams of finely-powdered  $\alpha\beta$ -dimethylanhydracetonebenzil were suspended in 70 c.c. of glacial acetic acid, and an acetic acid solution of 30 grams of chromium trioxide was gradually added, the oxidation being carried out in the cold as in the processes already described. The substance went into solution during the addition of the chromium trioxide; but by the next day a considerable quantity of a crystalline deposit had formed. After standing for 3 days, the mixture was diluted with water, and the crystalline precipitate was filtered off and washed with water, by which means it was obtained almost white. (The filtrate contains chiefly benzoic acid and may be rejected.) The precipitate was dissolved in ether and the ethereal solution was shaken with a solution of potassium carbonate, which left a neutral substance dissolved in the ether. On adding to the potassium carbonate extract a solution of sodium carbonate, the sparingly soluble sodium salt of the new acid was



precipitated; it was separated by filtration and decomposed by shaking it with dilute sulphuric acid and ether in a separating funnel. The aqueous filtrate from the sodium salt yields, on acidifying, a further quantity of the acid, but contaminated with benzoic acid; the latter may be removed by extraction with boiling light petroleum. The new acid was crystallised, first from ether, and then from a mixture of acetone and light petroleum. From either solvent it separates in short six-sided prisms with pointed ends. It melts, with decomposition, at  $164^{\circ}$ .

Analysis gave figures agreeing with the formula of  $\gamma$ -aceto- $\alpha$ -methyl-



0.1461 gave 0.3947  $\text{CO}_2$  and 0.0784  $\text{H}_2\text{O}$ . C = 73.67; H = 5.96.

0.1534 „ 0.4124  $\text{CO}_2$  „ 0.0808  $\text{H}_2\text{O}$ . C = 73.32; H = 5.85.

$\text{C}_{19}\text{H}_{18}\text{O}_4$  requires C = 73.55; H = 5.81 per cent.

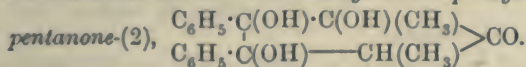
The silver salt was obtained as a white powder by precipitating the ammonium salt (itself only sparingly soluble in water) with silver nitrate.

0.2902 gave 0.0741 Ag. Ag = 25.5.

$\text{C}_{19}\text{H}_{17}\text{O}_4\text{Ag}$  requires Ag = 25.9 per cent.

The neutral substance remaining in the ether after the removal of the acid by potassium carbonate was deposited in large flat octahedral crystals. It may also be crystallised from hot alcohol or light petroleum. Its behaviour on melting is peculiar: it melts about  $89^{\circ}$  to a semi-opaque liquid, which clears about  $120^{\circ}$  with evolution of gas.

The specimens used for analysis were crystallised (1) from alcohol, (2) from ether, (3) from light petroleum. The figures obtained agreed with the formula of 1 : 3-dimethyl-4 : 5-diphenyl-1 : 4 : 5-trihydroxycyclopentanone-(2),



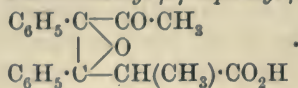
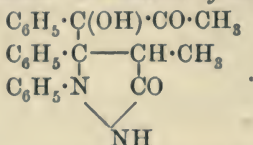
0.1355 gave 0.3608  $\text{CO}_2$  and 0.0802  $\text{H}_2\text{O}$ . C = 72.63; H = 6.58.

0.1640 „ 0.4364  $\text{CO}_2$  „ 0.0943  $\text{H}_2\text{O}$ . C = 72.57; H = 6.39.

0.1555 „ 0.4148  $\text{CO}_2$  „ 0.0900  $\text{H}_2\text{O}$ . C = 72.75; H = 6.43.

$\text{C}_{19}\text{H}_{20}\text{O}_4$  requires C = 73.08; H = 6.41 per cent.

Twenty grams of  $\alpha\beta$ -dimethylanhydracetonebenzil yielded, on oxidation, 4—5 grams of the acid and 6 grams of the neutral product.

A. *Reactions of  $\gamma$ -Aceto- $\alpha$ -methyl- $\beta$ - $\gamma$ -diphenyl- $\beta$ - $\gamma$ -oxidobutyric Acid,**Action of Phenylhydrazine: Formation of the Compound,*

—Three grams of acetomethyldiphenyloxidobutyric acid, 1 gram of phenylhydrazine, and a little alcohol were heated in a sealed tube at  $100^\circ$  for three hours. During the heating large crystals separated; these were filtered off, washed with alcohol and with ether, in which they were practically insoluble, and recrystallised from boiling benzene, from which the compound was deposited in colourless prisms melting, with decomposition, at  $212^\circ$ . It does not dissolve at  $100^\circ$  either in sodium hydroxide or in strong hydrochloric acid.

0.1606 gave 0.4385  $\text{CO}_2$  and 0.0897  $\text{H}_2\text{O}$ .  $\text{C} = 74.46$ ;  $\text{H} = 6.20$ .

0.1806 „ 11.4 c.c. moist nitrogen at  $16^\circ$  and 759 mm.  $\text{N} = 7.34$ .

$\text{C}_{25}\text{H}_{24}\text{O}_3\text{N}_2$  requires  $\text{C} = 75.00$ ;  $\text{H} = 6.00$ ;  $\text{N} = 7.00$  per cent.

Three grams of the acid yielded 3.2 grams of the compound melting at  $212^\circ$ .

The foregoing compound does not act further with phenylhydrazine at  $100^\circ$ , whilst at  $150^\circ$  there is considerable decomposition, crystals of ammonium carbonate being found in the tube. The product was not further examined.

*Oxime,*  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} - \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}_3 \\ | \quad \diagup \text{O} \\ \text{C}_6\text{H}_5 \cdot \text{C} - \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H} \end{array}$  .—To 2 grams of acetomethyl-

diphenyloxidobutyric acid, dissolved in an aqueous solution of 5 grams of potassium hydroxide, 1.8 grams (4 mol. proportions) of hydroxylamine hydrochloride were added, and the mixture was allowed to stand in the cold for 3 days. On acidifying the solution, a white precipitate was obtained; this was crystallised twice from a mixture of ether and light petroleum, and was thus obtained in spherical aggregates of slender needles, melting, with decomposition, at  $172$ – $173^\circ$ . It is soluble in sodium carbonate.

Analysis showed that the *oxime* of the acid had been formed:

0.1626 gave 0.4171  $\text{CO}_2$  and 0.0864  $\text{H}_2\text{O}$ .  $\text{C} = 69.95$ ;  $\text{H} = 5.90$ .

0.3543 „ 13.9 c.c. moist nitrogen at  $19^\circ$  and 760 mm.  $\text{N} = 4.51$ .

$\text{C}_{19}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C} = 70.15$ ;  $\text{H} = 5.84$ ;  $\text{N} = 4.30$  per cent.

The silver salt was obtained as a white precipitate by adding silver nitrate to a solution of the oxime in dilute ammonia :

0.3330 gave 0.0830 Ag.  $\text{Ag} = 24.92$ .

$\text{C}_{19}\text{H}_{18}\text{O}_4\text{NAg}$  requires  $\text{Ag} = 24.98$  per cent.

*Action of Heat: Formation of  $\beta$ -Aceto- $\alpha$ -ethyl- $\alpha\beta$ -diphenyloxidoethane,*  

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{CO} \cdot \text{CH}_3 \\ | \quad \diagup \quad \diagdown \\ \text{O} \\ | \quad \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}_2\text{H}_5 \end{array}$$
 .—A weighed quantity of acetomethyldiphenyloxido-

butyric acid was heated at its melting point ( $164^\circ$ ) in a small exhausted flask, connected with a Sprengel pump, until gas ceased to be evolved. The gas was pumped off, measured, and then absorbed by potassium hydroxide. It was found to be almost pure carbon dioxide and its amount corresponded almost exactly with the elimination of 1 mol. of that gas, as did also the loss in weight of the substance taken.

The product remaining in the flask solidified, on cooling, to a colourless, crystalline mass. It was dissolved in ether and the solution was extracted with potassium carbonate and sodium hydroxide; but these removed only a trace of acid. The neutral substance remaining on evaporation of the ether was crystallised from alcohol: it formed long four-sided needles, obliquely terminated, melting constantly at  $98\text{--}99^\circ$ . Analysis confirmed the above results as to the nature of the decomposition :

0.1470 gave 0.4360  $\text{CO}_2$  and 0.0914  $\text{H}_2\text{O}$ .  $\text{C} = 80.89$ ;  $\text{H} = 6.90$ .

0.1542 „ 0.4579  $\text{CO}_2$  „ 0.0954  $\text{H}_2\text{O}$ .  $\text{C} = 80.98$ ;  $\text{H} = 6.87$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2$  requires  $\text{C} = 81.20$ ;  $\text{H} = 6.76$  per cent.

The compound would be  $\beta$ -aceto- $\alpha$ -ethyl- $\alpha\beta$ -diphenyloxidoethane, assuming that, in the reaction in which it is formed, the elimination of carbon dioxide is not accompanied by any migration.

The mother liquor from this compound deposited a small quantity of rhombic prisms, which, without purification, melted at  $114\text{--}115^\circ$ . The quantity was insufficient for further examination.

The semicarbazone, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}(\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2) \cdot \text{CH}_3 \\ | \quad \diagup \quad \diagdown \\ \text{O} \\ | \quad \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}_2\text{H}_5 \end{array}$$
, of acetoethyl-  
 diphenyloxidoethane, was prepared by the method already described. It crystallised from alcohol in lustrous, small, thin plates melting at  $204^\circ$ .

0.1230 gave 13.7 c.c. moist nitrogen at  $10^\circ$  and 752 mm.  $\text{N} = 13.19$ .

$\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}_3$  requires  $\text{N} = 13.00$  per cent.

*Oxidation with Potassium Hypobromite: Formation of Methylidiphenyldihydroxyglutaric Acid,*  

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H} \end{array}$$
 .—Three grams



of acetomethyldiphenyloxidobutyric acid were added to a solution of potassium carbonate. The sparingly soluble potassium salt separated.\* The mixture was gently warmed on the water-bath, and a solution of potassium hypobromite (prepared by dissolving 6 grams of bromine in a solution of 7 grams of potassium hydroxide in 30 c.c. of water) was gradually added, the warming being continued for half-an-hour. The potassium salt went into solution, and a strong smell of bromoform was noticeable, whilst a small quantity of a heavy liquid separated; the latter crystallised on cooling, but the quantity was insufficient for examination. The filtered solution was treated with sulphur dioxide and acidified. The acid, thus precipitated, was recrystallised from a mixture of ether and ligroin, and showed all the properties of *methyldiphenyldihydroxyglutaric acid*, a compound already obtained by the oxidation of  $\beta$ -methylanthracetonebenzil (*v. supra*). Like this substance it forms obliquely-terminated, four-sided prisms, with an extinction angle of  $22^\circ$  in polarised light, and melts, with decomposition, at  $176^\circ$ . Mixed with a sample of the acid prepared from  $\beta$ -methylanthracetonebenzil, it showed no depression of melting point. Analysis gave confirmatory results.

0.1652 gave 0.3972  $\text{CO}_2$  and 0.0846  $\text{H}_2\text{O}$ . C = 65.57; H = 5.69.

0.1631 „ 0.3906  $\text{CO}_2$  „ 0.0829  $\text{H}_2\text{O}$ . C = 65.31; H = 5.64.

$\text{C}_{18}\text{H}_{18}\text{O}_6$  requires C = 65.45; H = 5.45 per cent.

The yield is very good.

By conducting the foregoing oxidation in the cold, a complex mixture of acids was obtained, one of which, at least, contained bromine. These products were not further examined.

*Action of Hydriodic Acid: Formation of Methyldiphenyl- $\Delta^1$ -croto-*

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5\cdot\text{CH} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5\cdot\text{C}=\text{C}\cdot\text{CH}_3 \end{array}$$

*lactone*, —Four grams of acetomethyldiphenyloxidobutyric acid were boiled with excess of fuming hydriodic acid for 3 minutes. The product was washed with water, dissolved in ether, and treated with sulphurous acid and potassium carbonate solution. The latter extracted only a small quantity of an acid which crystallised from ether in thin, rectangular plates melting about  $170^\circ$  with decomposition; there was not sufficient for further examination. The neutral substance remaining in the ether was deposited in clear, thick crystals, of rhombic outline; they melted at  $88.5^\circ$  and proved to be *methyldiphenyl- $\Delta^1$ -croto lactone*, a substance already obtained in other reactions in the course of the present work. Their identity was further established

\* It would doubtless have been better to have used the readily soluble sodium salt, and to have oxidised with sodium hypobromite.

by the mixture melting-point method, a specimen of the synthetic compound (from  $\alpha$ -desylpropionic acid, *v. infra*) being employed for comparison, and also by analysis.

0.1575 gave 0.4721  $\text{CO}_2$  and 0.0817  $\text{H}_2\text{O}$ .  $\text{C} = 81.74$ ;  $\text{H} = 5.76$ .

$\text{C}_{17}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 81.60$ ;  $\text{H} = 5.60$  per cent.

The yield was about 2 grams.

In order to obtain the corresponding acid, the lactone was warmed with alcoholic potassium hydroxide. The acid, liberated from its salt, crystallised from alcohol in flat needles melting, with decomposition, at  $220^\circ$ . It proved to be identical with Knœvenagel's  $\alpha$ -desylpropionic

acid,  $\text{C}_6\text{H}_5 \cdot \overset{\text{CO}}{\underset{|}{\text{C}}} \cdot \text{CH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}$ , which this investigator prepared by acting with ethyl  $\alpha$ -bromopropionate on sodium deoxybenzoin, and hydrolysing the ester thus obtained (*Ber.*, 1888, 21, 1353). Knœvenagel gives the melting point of his acid as  $213\text{--}215^\circ$ ; but a specimen, which we prepared by his method, melted, as above, at  $220^\circ$ , and, when mixed with the acid from the lactone, showed no depression of melting point. Much, however, depends upon the rate of heating, as, in the neighbourhood of its melting point, the acid is gradually transformed into the lactone, and shows signs of softening even as low as  $200^\circ$ .

The acid prepared from the lactone gave figures agreeing with the formula of  $\alpha$ -desylpropionic acid.

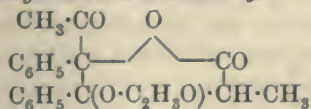
0.1600 gave 0.4444  $\text{CO}_2$  and 0.0886  $\text{H}_2\text{O}$ .  $\text{C} = 75.75$ ;  $\text{H} = 6.15$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 76.11$ ;  $\text{H} = 5.97$  per cent.

A specimen of  $\alpha$ -desylpropionic acid prepared by Knœvenagel's method was distilled under reduced pressure. The temperature of the bath was slowly raised to  $255\text{--}260^\circ$ , when the substance passed over. The distillate was dissolved in ether, and the solution deposited clear thick rhombs of *methyldiphenyl- $\Delta^1$ -crotolactone* melting at  $88.5^\circ$ . As already mentioned, the melting point was not depressed when the substance was mixed with the lactone prepared by the action of hydriodic acid on acetomethyldiphenyloxidobutyric acid.

If  $\alpha$ -desylpropionic acid were treated in the cold with acetic anhydride containing a few drops of sulphuric acid, it ought to yield the labile *methyldiphenyl- $\Delta^2$ -crotolactone* (not yet prepared); but we did not try this experiment as we wished to avoid trenching on Thiele's work in this field.

*Action of Acetic Anhydride: Formation of the Lactone,*



(*m. p.*  $140^\circ$ ).—Four grams of acetomethyldiphenyloxidobutyric acid

were added to 32 c.c. of acetic anhydride with which 8 drops of concentrated sulphuric acid had previously been mixed. The substance readily dissolved. After standing for a day at ordinary temperature, the mixture was poured into excess of water. The precipitate was filtered off and dissolved in ether. Potassium carbonate removed only a trace of acid. On evaporation of the ether, the neutral substance, which proved to be an *acetoxy-lactone* of the formula above given, was deposited in short, four- or six-sided prisms. Recrystallised from a mixture of benzene and ligroin, it melted constantly at  $140^{\circ}$ . The yield was about 1 gram.

0.1606 gave 0.4216  $\text{CO}_2$  and 0.0828  $\text{H}_2\text{O}$ .  $\text{C} = 71.59$  ;  $\text{H} = 5.72$ .

0.1596 „ 0.4173  $\text{CO}_2$  „ 0.0827  $\text{H}_2\text{O}$ .  $\text{C} = 71.30$  ;  $\text{H} = 5.75$ .

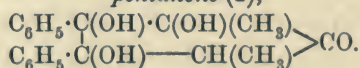
$\text{C}_{21}\text{H}_{20}\text{O}_5$  requires  $\text{C} = 71.59$  ;  $\text{H} = 5.68$  per cent.

The foregoing compound, when warmed with alcoholic potassium hydroxide, yielded  *$\alpha$ -desylpropionic acid* (m. p.  $220^{\circ}$ , with decomposition), which was identified by its properties, by the mixture melting-point test, and by analysis.

0.1570 gave 0.4403  $\text{CO}_2$  and 0.0859  $\text{H}_2\text{O}$ .  $\text{C} = 76.48$  ;  $\text{H} = 6.07$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 76.11$  ;  $\text{H} = 5.97$  per cent.

B. *Reactions of 1 : 3-Dimethyl-4 : 5-diphenyl-1 : 4 : 5-trihydroxycyclopentanone-(2),*



*Semicarbazone*.—The *semicarbazone* of dimethyldiphenyltrihydroxycyclopentanone, the neutral oxidation product of  $\alpha\beta$ -dimethylanhydracetonebenzil, was prepared in the cold by the method already described. It crystallised from alcohol in slender needles, melting very indefinitely between  $165^{\circ}$  and  $180^{\circ}$  with decomposition.

0.1589 gave 16.2 c.c. moist nitrogen at  $16^{\circ}$  and 748 mm.  $\text{N} = 11.69$ .

$\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_3$  requires  $\text{N} = 11.38$  per cent.

*Action of Hydroxylamine*.—An alcoholic solution of 1 gram of dimethyldiphenyltrihydroxycyclopentanone was mixed with a concentrated aqueous solution of 0.66 gram (3 mols.) of hydroxylamine hydrochloride, and 0.5 gram of finely powdered anhydrous sodium carbonate was added. The mixture was allowed to stand for 9 days in the cold. The solution was then filtered from the precipitate of sodium chloride and diluted with water until a turbidity was produced. On standing, the liquid deposited crystals of a substance which, after recrystallisation from a mixture of ether and light petroleum, was



obtained in laminæ of rhombic outline, melting with decomposition at 185°.

Analysis gave figures pointing to the formula  $C_{19}H_{24}O_5N_2$ .

0.1910 gave 0.4400  $CO_2$  and 0.1159  $H_2O$ . C = 62.82; H = 6.74.

0.2208 gave 14.8 c.c. moist nitrogen at 15° and 752 mm. N = 7.76.

$C_{19}H_{24}O_5N_2$  requires C = 63.33; H = 6.66; N = 7.77 per cent.

The compound is formed according to the equation



only one mol. of water being eliminated. Probably the *cyclopentane* ring opens in the process; but, even then, it is difficult to reconcile the constitution of a dimethyldiphenyltrihydroxycyclopentanone, which we ascribe to the compound  $C_{19}H_{20}O_4$ , with the formation of this hydroxylamine derivative.

The foregoing experiment was repeated, substituting potassium acetate for sodium carbonate, but only an uncrystallisable gum was obtained.

*Attempt to Oxidise Dimethyldiphenyltrihydroxycyclopentanone by means of Chromium Trioxide to Acetomethyldiphenyloxidobutyric Acid.*—We record this negative result because it is of importance as showing that dimethyldiphenyltrihydroxycyclopentanone is not an intermediate product in the oxidation of  $\alpha\beta$ -dimethylanhydracetonebenzil to acetomethyldiphenyloxidobutyric acid (*v. supra*).

The *cyclopentanone* derivative and the chromium trioxide, dissolved in glacial acetic acid, were in one case allowed to stand in the cold for a fortnight and, in another, warmed on the water-bath for 10 minutes. In the first case there was no action at all; in the second, a little benzoic acid was formed, but the greater part of the *cyclopentanone* derivative was recovered unchanged.

*Action of Hydriodic Acid.*—Five grams of dimethyldiphenyltrihydroxycyclopentanone were boiled with excess of fuming hydriodic acid for 2 minutes. The product was dissolved in ether and successively treated with sulphurous acid and sodium carbonate solution. The latter removed an acid—the chief product of the reaction—which crystallised from alcohol in flat, lustrous, prismatic needles melting at 215–216°. (Yield: 2.6 grams.)

Analysis gave figures agreeing with the formula  $C_{19}H_{18}O_2$ .

0.1605 gave 0.4801  $CO_2$  and 0.0974  $H_2O$ . C = 81.58; H = 6.74.

0.1472 gave 0.4406  $CO_2$  and 0.0884  $H_2O$ . C = 81.63; H = 6.67.

$C_{19}H_{18}O_2$  requires C = 82.01; H = 6.47 per cent.

The acid is formed according to the equation



The *silver* salt was obtained as a white precipitate by adding silver nitrate to the ammonium salt.

0.4611 gave 0.1268 Ag.  $\text{Ag} = 27.49$ .

$\text{C}_{19}\text{H}_{17}\text{O}_2$  Ag requires  $\text{Ag} = 28.02$  per cent.

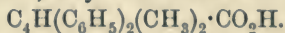
A solution of the acid in sodium carbonate is stable towards permanganate in the cold.

A solution of the acid in glacial acetic acid decolorised a solution of bromine in the same solvent. The weight of the additive compound obtained from 2 grams of acid was 3 grams, showing that a *dibromide* had been formed. The dibromide, recrystallised from a mixture of ether and light petroleum, melted, with decomposition, at  $114^\circ$ ; but as it turned yellow when we attempted to purify it, and was evidently decomposing, we did not attempt to analyse it.

On warming a solution of the acid in potassium carbonate with potassium hypobromite, a small quantity of an uncrystallisable neutral compound was formed; but the greater part of the acid was recovered unchanged.

Sodium in boiling alcohol is without action on the acid; neither did boiling for 4 hours with hydriodic acid and amorphous phosphorus alter it. By heating it however with this mixture at  $150^\circ$  for 8 hours, a neutral substance and an acid were obtained, neither of which, however, could be induced to crystallise.

The formula of an acid,  $\text{C}_{19}\text{H}_{18}\text{O}_2$ , formed from dimethyldiphenyltrihydroxycyclopentanone, may be resolved into



If the unresolved group  $\text{C}_4$  is an open chain, it must contain either one set of triple bonds, or two sets of double bonds, neither of which constitutions would be in harmony with the stability of the acid towards both reducing and oxidising agents, especially towards permanganate. It is more probable, therefore, that this  $\text{C}_4$  is a cyclobutene group; and, on this assumption, a possible constitution for

the acid would be  $\text{C}_6\text{H}_5 \cdot \overset{\text{C}}{\underset{\text{C}}{\text{C}}}(\text{CH}_3) \cdot \text{CO}_2\text{H}$ . It would be necessary to

assume that the pentacarbon ring of dimethyldiphenyltrihydroxycyclopentanone opens, and then closes again, forming a tetracarbon ring. The formula would account for the stability of the acid towards permanganate, as there is no hydrogen attached to the doubly-linked carbon atoms (compare *Trans.*, 1897, 71, 129), and also for the formation of a dibromide.

The original ethereal solution of the crude reduction product, from which the foregoing acid had been removed by sodium carbonate, left, on evaporation, a crystalline residue, which, by treatment with alcohol, was separated into the two following substances:

1. Needles (0.3 gram), melting at  $175^{\circ}$  and showing straight extinction in polarised light. On attempting to recrystallise the substance from alcohol, benzene, or ether, it was deposited in a pulverulent form. It appears to be identical with the compound  $C_{19}H_{16}O_2$  (m. p.  $178^{\circ}$ ) obtained by the action of acetic anhydride, with the addition of a few drops of sulphuric acid, on dimethyldiphenyltrihydroxycyclopentanone (*v. infra*). Mixed with a little of the compound  $C_{19}H_{16}O_2$ , it still melted at  $175^{\circ}$ . The low melting point of the present preparation is due to the fact that there was not sufficient substance for complete purification.

2. Four-, six-, or eight-sided laminæ (0.6 gram), which, on recrystallisation, melted at  $122^{\circ}$ . This substance was proved, by the mixture melting-point test, to be identical with *dimethyldiphenylcyclopentenone*,  $\begin{array}{c} C_6H_5 \cdot C \cdot CH(CH_3) \\ | \\ C_6H_5 \cdot C \cdot CH(CH_3) \end{array} > CO$  (obtained by the reduction of  $\alpha\beta$ -dimethylanhydracetonebenzil with hydriodic acid, and to be described, along with its derivatives, in a subsequent communication). Analysis confirmed this result.

0.1559 gave 0.4953  $CO_2$  and 0.0969  $H_2O$ .  $C = 86.64$ ;  $H = 6.90$ .

$C_{19}H_{16}O$  requires  $C = 87.02$ ;  $H = 6.87$  per cent.

*Action of Acetic Anhydride.*—Five grams of finely powdered dimethyldiphenyltrihydroxycyclopentanone were added to a mixture of 8 c.c. of acetic anhydride and 2 drops of concentrated sulphuric acid. The substance rapidly dissolved, the temperature rising and the solution becoming dark-coloured. On standing, the solution deposited thick prisms; the liquid was poured off from the crystals and mixed with water. Both the crystals and the precipitated solid yielded, on recrystallisation from alcohol, long needles showing straight extinction in polarised light and melting at  $178^{\circ}$ . The substance usually crystallises well from alcohol, ether, benzene or light petroleum, but is sometimes deposited in a pulverulent form. (Yield 2.9 grams.)

0.1640 gave 0.4976  $CO_2$  and 0.0878  $H_2O$ .  $C = 82.74$ ;  $H = 5.94$ .

0.1569 „ 0.4758  $CO_2$  „ 0.0834  $H_2O$ .  $C = 82.70$ ;  $H = 5.90$ .

$C_{19}H_{16}O_2$  requires  $C = 82.61$ ;  $H = 5.80$  per cent.

Warmed with alcoholic potassium hydroxide, the foregoing compound yields an acid; but the yield is very poor, and the chief product is a dark-coloured amorphous mass. The reaction was not further studied.

*Action of Potassium Hydroxide.*—Five grams of dimethyldiphenyltrihydroxycyclopentanone were dissolved in 50 c.c. of cold 5 per cent. alcoholic potassium hydroxide, and the solution, which was yellow, was allowed to remain at the ordinary temperature for 20 minutes,



after which it was diluted with water. The solution, which remained clear, was then saturated with carbon dioxide; this precipitated a viscid substance which was removed with ether; and the remaining aqueous solution gave, on acidifying with hydrochloric acid, no further precipitate. The ethereal solution, when concentrated, deposited a solid substance; this was powdered, filtered, and washed with a mixture of ether and light petroleum to remove oil and a pink colouring matter; and the residue, which weighed 4 grams, was recrystallised from methyl alcohol. It crystallised in colourless, large, flat, six-sided prisms, usually hollow; also in large tabular crystals like flat octahedra. Both forms melted at  $89-90^\circ$ . Analysis showed that the substance had the formula  $C_{19}H_{18}O_3$ , having been formed from dimethyldiphenyltrihydroxycyclopentanone by abstraction of a molecule of water.

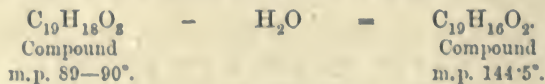
0.1563 gave 0.4428  $CO_2$  and 0.0864  $H_2O$ .  $C = 77.26$ ;  $H = 6.14$ .

$C_{19}H_{18}O_3$  requires  $C = 77.55$ ;  $H = 6.12$  per cent.

By allowing the solution of dimethyldiphenyltrihydroxycyclopentanone in alcoholic potassium hydroxide to remain for several days, and then evaporating off the alcohol in a vacuum desiccator over sulphuric acid, the compound  $C_{19}H_{18}O_3$  (m.p.  $89-90^\circ$ ), which is formed in the first instance, is decomposed, and ethyl phenyl ketone and potassium benzoate are obtained in its place. This decomposition is, however, better effected with the aid of boiling aqueous potassium hydroxide (*v. infra*).

By oxidising the compound  $C_{19}H_{18}O_3$  (m.p.  $89-90^\circ$ ), with chromium trioxide in acetic acid solution, benzoic acid and an oil smelling of ethyl phenyl ketone were also obtained.

One gram of the compound  $C_{19}H_{18}O_3$  (m.p.  $89-90^\circ$ ) was boiled with fuming hydriodic acid for 5 minutes. The product, treated in the usual way, yielded a compound crystallising from ether or alcohol in oblique tables, usually with one of the corners truncated, melting at  $144.5^\circ$ . It is not affected by alcoholic potassium hydroxide even when heated with it on the water-bath for 4 hours. Analysis showed that it had been formed according to the equation



the hydriodic acid having had a dehydrating, not a reducing, action.

0.1586 gave 0.4791  $CO_2$  and 0.0830  $H_2O$ .  $C = 82.38$ ;  $H = 5.81$ .

0.1585 „ 0.4793  $CO_2$  „ 0.0832  $H_2O$ .  $C = 82.47$ ;  $H = 5.83$ .

$C_{19}H_{16}O_2$  requires  $C = 82.61$ ;  $H = 5.80$  per cent.

In order to study the more exhaustive action of potassium hydroxide on dimethyldiphenyltrihydroxycyclopentanone, 6 grams of this substance were heated in a distilling flask with a dilute aqueous solution of 6 grams of potassium hydroxide. Drops of a clear oil passed over with the aqueous distillate. As soon as the oil ceased to distil over, the process was interrupted. The solution remaining in the distilling flask contained a crystalline matter in suspension; this was collected and purified by recrystallisation, first from a mixture of benzene and light petroleum, afterwards from alcohol. It formed oblique tables, sometimes with the acute corners truncated, and melted at  $144.5^{\circ}$ . It was identical with the compound  $C_{19}H_{16}O_2$ , just described, as was proved both by the mixture melting-point test and by analysis.

0.1789 gave 0.5387  $CO_2$  and 0.0952  $H_2O$ .  $C = 82.12$ ;  $H = 5.91$ .

$C_{19}H_{16}O_2$  requires  $C = 82.61$ ;  $H = 5.80$ .

The yield of this substance was small.

On acidifying the alkaline filtrate a considerable quantity of benzoic acid was precipitated.

The oil, above referred to, was extracted from the aqueous distillate with ether, the ethereal solution was dried with calcium chloride, and, after expelling the ether, the oil was distilled under reduced pressure. It proved to be *ethyl phenyl ketone*. Placed in a refrigerator it solidified to a mass of crystals which melted at  $17^{\circ}$ . A specimen of ethyl phenyl ketone, obtained from Kahlbaum and further purified by distillation under reduced pressure, was cooled with water and then touched with a crystal of the foregoing substance. It crystallised instantly, and the crystals melted at  $18^{\circ}$ . A mixture of the two specimens melted also at  $18^{\circ}$ . Analysis of the substance obtained in the present reaction gave figures agreeing with the formula of ethyl phenyl ketone.

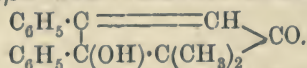
0.1710 gave 0.5047  $CO_2$  and 0.1158  $H_2O$ .  $C = 80.49$ ;  $H = 7.52$ .

$C_9H_{10}O$  requires  $C = 80.60$ ;  $H = 7.46$ .

In the action of hot aqueous potassium hydroxide on dimethyldiphenyltrihydroxycyclopentanone there are evidently two reactions: one in which the compound  $C_{19}H_{16}O_2$  is formed from the whole molecule by abstraction of two mols. of water, this compound, when once formed, being quite stable towards potassium hydroxide; and another in which the molecule of the original substance is broken up, yielding benzoic acid and ethyl phenyl ketone. It is probable that one of the primary products of hydrolysis is  $\alpha$ -benzoylpropionic acid  $C_6H_5 \cdot CO \cdot CH(CH_3) \cdot CO_2H$ , as may be seen by inspection of the constitutional formula of dimethyldiphenyltrihydroxycyclopentanone; and

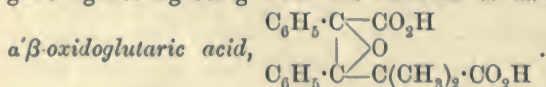
that this  $\beta$ -ketonic acid then parts with carbon dioxide, yielding ethyl phenyl ketone; but even  $\alpha$ -benzoylpropionic acid and benzoic acid together would not account for more than 17 out of the 19 carbon atoms of the original compound. We were, however, unable to discover any further product of decomposition.

IV.  $\beta\beta$ -DIMETHYLANHYDRACETONEBENZIL,



*Oxidation of  $\beta\beta$ -Dimethylanhydracetonebenzil with Chromium Trioxide.*

Twenty grams of finely powdered  $\beta\beta$ -dimethylanhydracetonebenzil were suspended in 70 c.c. of glacial acetic acid, and a solution of 30 grams of chromium trioxide in the same solvent was gradually added, the mixture being cooled with water during the process. The suspended substance went into solution during the addition of the chromium trioxide; but in the course of a few hours a large quantity of a crystalline deposit had formed. After standing overnight the mixture was filtered, and the solid was washed, first with glacial acetic acid and then with water. The product is almost white. A further quantity can be obtained by precipitating the acetic acid filtrate with water and extracting with ether. The substance obtained by these processes was dissolved in potassium carbonate, and the solution was filtered from unaltered substance. The filtrate was then warmed for several hours on the water-bath, filtered from chromium compounds, and acidified. The precipitated acid was purified by recrystallisation from a mixture of ethyl acetate and light petroleum, from which it is deposited in sheaves of slender needles. (Yield 13–14 grams.) The acid appears to be dimorphous: when freshly crystallised it melts with decomposition at  $171^\circ$ ; but after the substance has stood for several weeks, the melting point is found to have risen to  $184^\circ$ . Analysis gave figures agreeing with the formula of *aa-dimethyl- $\alpha'\beta$ -diphenyl-*



0.1620 gave 0.4147  $\text{CO}_2$  and 0.0824  $\text{H}_2\text{O}$ . C = 69.81; H = 5.65.

0.1581 „ 0.4044  $\text{CO}_2$  „ 0.0802  $\text{H}_2\text{O}$ . C = 69.76; H = 5.63.

$\text{C}_{19}\text{H}_{18}\text{O}_6$  requires C = 69.93; H = 5.52 per cent.

For analysis it was found necessary to recrystallise the acid repeatedly from the mixture of ethyl acetate and light petroleum, otherwise the value for carbon was found too low.



The silver salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt.

0.3931 gave 0.1561 Ag.  $\text{Ag} = 39.70$ .

$\text{C}_{19}\text{H}_{16}\text{O}_5\text{Ag}_2$  requires  $\text{Ag} = 39.98$  per cent.

Both the potassium and the sodium salts are sparingly soluble in water.

The acid is fairly stable towards oxidising agents: thus its solution in sodium carbonate is not altered by warming it either with potassium permanganate, or with potassium hypobromite. Warming with a solution of chromium trioxide in acetic acid converts it, however, into a neutral compound, crystallising from a mixture of ether and light petroleum in needles melting at  $99-100^\circ$ , which has not yet been further investigated.

*Action of Phenylhydrazine on Dimethyldiphenyloxidoglutaric Acid:*

*Formation of the Compound*  $\text{NH} \begin{matrix} \text{CO} \text{---} \text{C}(\text{C}_6\text{H}_5) \cdot \text{O} \cdot \text{CO} \\ \text{N}(\text{C}_6\text{H}_5) \cdot \text{C}(\text{C}_6\text{H}_5) \text{---} \text{C}(\text{CH}_3)_2 \end{matrix}$ —

1.8 grams of the acid were dissolved in a little alcohol and heated in a sealed tube at  $100^\circ$  for 3 hours with 0.8 gram phenylhydrazine. On cooling, colourless plates (1 gram) separated, and a further quantity was obtained from the mother liquor on acidifying with acetic acid and diluting with water. The compound crystallises from ether or alcohol in large, colourless, six- or eight-sided plates, melting, without decomposition, at  $182^\circ$ . Analysis gave figures agreeing with the formula  $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$ .

0.1559 gave 0.4300  $\text{CO}_2$  and 0.0776  $\text{H}_2\text{O}$ .  $\text{C} = 75.22$ ;  $\text{H} = 5.53$ .

0.1849 „ 11.6 c.c. moist nitrogen at  $16^\circ$  and 757 mm.  $\text{N} = 7.28$ .

$\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$  requires  $\text{C} = 75.37$ ;  $\text{H} = 5.52$ ;  $\text{N} = 7.03$  per cent.

The compound is insoluble in sodium carbonate, but if evaporated to dryness with alcoholic potassium hydroxide, it forms a salt which is soluble in water. The acid, when freshly precipitated from this salt by dilute sulphuric acid, is soluble in sodium carbonate; but, on drying, it becomes insoluble in the carbonate solution, and, when recrystallised from alcohol, is converted into the plates or laminæ of the foregoing compound  $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$ , melting at  $182^\circ$ . The substance was further identified by the mixture melting-point test.

The  $\gamma$ -lactone ring thus opens under the influence of the caustic alkali, and a salt of the corresponding acid is formed; but the liberated acid is unstable and readily passes back into the lactone.

*Action of Heat on Dimethyldiphenyloxidoglutaric Acid: Formation*

*of its Anhydride,*  $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}(\text{CH}_3)_2 \text{---} \text{CO} \end{matrix}$  O.—In order to ascertain the

nature of the decomposition which dimethyldiphenyloxidoglutaric acid underwent when heated, 2 grams of the substance were distilled at a pressure of about 12 mm. When the temperature of the oil-bath was 230—240°, the product of the action of heat distilled over, solidifying in the receiver. By recrystallisation from a mixture of benzene and light petroleum it was obtained in slender needles melting at 158°. Analysis showed that it had been formed from the acid by abstraction of a molecule of water :

0.1536 gave 0.4160 CO<sub>2</sub> and 0.0731 H<sub>2</sub>O. C = 73.86 ; H = 5.28.

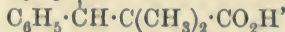
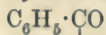
0.1645 „ 0.4446 CO<sub>2</sub> „ 0.0774 H<sub>2</sub>O. C = 73.71 ; H = 5.22.

C<sub>19</sub>H<sub>16</sub>O<sub>4</sub> requires C = 74.02 ; H = 5.19 per cent.

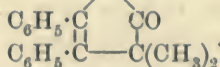
It is insoluble in hot aqueous sodium hydroxide ; but, by evaporating its solution in alcoholic potassium hydroxide to dryness, a residue was obtained which dissolved completely in water. On acidifying the solution, *dimethyldiphenyloxidoglutaric acid* was obtained, which was identified both by its physical properties and by the mixture melting-point test. The compound C<sub>19</sub>H<sub>16</sub>O<sub>4</sub> is therefore, as above formulated, the *anhydride* of this acid.

*Action of Acetic Anhydride on Dimethyldiphenyloxidoglutaric Acid : Formation of Dimethyldiphenyloxidoglutaric Anhydride.*—One gram of the acid was dissolved in the cold in 15 c.c. of acetic anhydride to which 4 drops of concentrated sulphuric acid had been added. In a short time hair-like needles separated, which melted at 158°. The mother liquor, on dilution with water, gave a precipitate of the same substance, which, after crystallisation from a mixture of benzene and light petroleum, showed the same melting point. It was identical with the foregoing *anhydride* obtained by the action of heat on the acid, as was further proved by the mixture melting-point test.

*Action of Hot Dilute Sulphuric Acid on Dimethyldiphenyloxidoglutaric Acid : Formation of Dimethyldiphenyloxidoglutaric Anhydride, α-Desyl-isobutyric Acid,*



*phenyl-Δ<sup>2</sup>-crotolactone,*



—One gram of dimethyldiphenyloxidoglutaric acid was boiled for an hour with dilute sulphuric acid (1 : 1). On dissolving the product in ether and extracting with sodium carbonate, a small quantity of an acid was obtained, which, after crystallisation from alcohol, melted at 218° with decomposition. (It was afterwards shown to be *α-desylisobutyric acid*.) The neutral part was dissolved in benzene, and light petroleum was added : slender

needles were deposited, melting at  $158^{\circ}$  (*dimethyldiphenyloxidoglutaric anhydride*). The mother liquor yielded rhombs melting at  $105-106^{\circ}$ .

Five grams of dimethyloxidoglutaric acid were then boiled with dilute sulphuric acid (1:1) for 6 hours. This time none of the anhydride was obtained: the product yielded 0.2 grams of  $\alpha$ -desylisobutyric acid (m. p.  $218^{\circ}$ ) and 3.5 grams of the neutral compound crystallising in rhombs (m. p.  $105-106^{\circ}$ ). The latter substance crystallises well from alcohol, or from a mixture of benzene and light petroleum. On analysis it gave figures agreeing with those required for *dimethyldiphenylcrotonolactone*:

0.1582 gave 0.4746  $\text{CO}_2$  and 0.0873  $\text{H}_2\text{O}$ . C = 81.81; H = 6.13.

$\text{C}_{15}\text{H}_{16}\text{O}_2$  requires C = 81.81; H = 6.06 per cent.

*Action of Alcoholic Potassium Hydroxide on Dimethyldiphenylcrotonolactone: Formation of  $\alpha$ -Desylisobutyric Acid.*—Two grams of the foregoing dimethyldiphenylcrotonolactone (m. p.  $105-106^{\circ}$ ) were heated on the water-bath with excess of 5 per cent. alcoholic potassium hydroxide until the alcohol was expelled. The residue dissolved completely in water, and, on acidifying, an acid was obtained which, after recrystallisation from alcohol, formed flat needles melting at  $218^{\circ}$  with decomposition. It was identical with the acid of the same melting point obtained in small quantity by boiling dimethyldiphenyloxidoglutaric acid with dilute sulphuric acid. Analysis showed that, in the present reaction, it had been formed from dimethyldiphenylcrotonolactone by assumption of the elements of a molecule of water. It thus has the composition of  $\alpha$ -desylisobutyric acid.

0.1555 gave 0.4349  $\text{CO}_2$  and 0.0918  $\text{H}_2\text{O}$ . C = 76.27; H = 6.55.

$\text{C}_{15}\text{H}_{18}\text{O}_3$  requires C = 76.59; H = 6.38 per cent.

As the acid did not dissolve well in dilute ammonia, it was boiled with a solution of sodium carbonate, keeping the acid in excess. On adding silver nitrate to the filtered solution the *silver* salt was obtained as a white precipitate.

0.4901 gave 0.1352 Ag. Ag = 27.58.

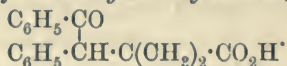
$\text{C}_{15}\text{H}_{17}\text{O}_3$  Ag requires Ag = 27.75 per cent.

*Synthesis of  $\alpha$ -Desylisobutyric Acid.*—In order to prove conclusively that the foregoing acid had the constitution here assigned to it, it was synthesised by the following reaction—an application of Knoevenagel's process, already referred to, for the preparation of desyl-fatty acids.

1.2 grams of sodium were dissolved in 12 grams of absolute alcohol. The solution of the ethoxide solidified on cooling. Ten



grams of deoxybenzoin were then added, which caused the mixture to liquefy. The flask was then cooled with ice, and 10 grams of ethyl  $\alpha$ -bromoisobutyrate were gradually added. The mixture was allowed to stand for 3 hours in the cold, after which it was heated on the water-bath for a few minutes, employing a reflux condenser. Excess of 10–15 per cent. aqueous potassium hydroxide was then added, and the heating was continued for 2 hours, so as to hydrolyse the new ester. When cool, the mixture was diluted with water and extracted with ether: this removed 3 grams of unchanged deoxybenzoin. The aqueous solution was acidified, and the oily precipitate was separated and dissolved in ammonia. The filtered ammoniacal solution, on acidifying, gave a semi-solid precipitate; by recrystallisation from alcohol the substance was obtained in flat needles melting, with decomposition, at  $218^{\circ}$ . It agreed in all its physical properties with the acid obtained by boiling dimethyldiphenyloxidoglutaric acid with dilute sulphuric acid and by the action of potassium hydroxide on dimethyldiphenylcrotonolactone, and the identity was further proved by the mixture melting-point test. From its formation in the present reaction it can only be  *$\alpha$ -desylisobutyric acid*,



Analysis gave figures agreeing with this formula.

0.1595 gave 0.4474  $\text{CO}_2$  and 0.0919  $\text{H}_2\text{O}$ .  $\text{C} = 76.50$ ;  $\text{H} = 6.40$ .

$\text{C}_{18}\text{H}_{18}\text{O}_3$  requires  $\text{C} = 76.59$ ;  $\text{H} = 6.38$  per cent.

The yield of pure substance was only 1.5 grams.

*Conversion of  $\alpha$ -Desylisobutyric Acid into Dimethyldiphenylcrotonolactone.*—0.3 gram of the acid, obtained by hydrolysis of dimethyldiphenylcrotonolactone with potassium hydroxide, was dissolved in the cold in 2.5 c.c. of acetic anhydride containing 1 drop of concentrated sulphuric acid, and the mixture was allowed to stand for 24 hours. It was then poured into water, and the crystalline precipitate was separated by filtration and dissolved in ether. No acid could be extracted from the ethereal solution by sodium carbonate. The neutral substance crystallised in rhombs melting at  $105$ – $106^{\circ}$ , and was identical with the *dimethyldiphenylcrotonolactone* obtained as already described from dimethyldiphenyloxidoglutaric acid, a result which was confirmed by the mixture melting-point test.

0.1588 gave 0.4762  $\text{CO}_2$  and 0.0880  $\text{H}_2\text{O}$ .  $\text{C} = 81.78$ ;  $\text{H} = 6.15$ .

$\text{C}_{18}\text{H}_{16}\text{O}_2$  requires  $\text{C} = 81.81$ ;  $\text{H} = 6.06$  per cent.

*Action of Hydriodic Acid on Dimethyldiphenyloxidoglutaric Acid.*—Two grams of dimethyldiphenyloxidoglutaric acid were boiled for 2

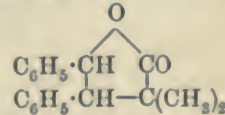
minutes with excess of fuming hydriodic acid. The product was dissolved in ether, and the solution was treated with sulphurous acid and extracted with sodium carbonate solution. This removed 1 gram of a mixture of acids, which was separated by crystallisation into unchanged acid and *α*-desylisobutyric acid (m. p. 218°). The latter gave, on analysis, figures agreeing with the formula.

0.1581 gave 0.4419 CO<sub>2</sub> and 0.0910 H<sub>2</sub>O. C = 76.22; H = 6.39.

C<sub>13</sub>H<sub>18</sub>O<sub>2</sub> requires C = 76.59; H = 6.38 per cent.

The neutral portion of the product, remaining on evaporation of the ethereal solution, was crystallised from alcohol. It yielded flat prisms melting at 106° (see the following experiment) and a small quantity of lustrous, six- or eight-sided laminæ melting at 96°. We were unable to identify the latter substance.

In a second experiment a mixture of 5 grams of dimethyldiphenyl-oxidoglutaric acid, 75 grams of hydriodic acid (sp. gr. 1.7), and 5 grams of red phosphorus, was boiled for 3 hours, using a reflux condenser. The organic product was treated as in the foregoing experiment. Sodium carbonate extracted from the ethereal solution an acid which was deposited from alcohol in short prisms melting at 172° (yield: 0.35 gram) and which was subsequently shown to be *αα*-dimethyl-*βγ*-diphenylbutyric acid, C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>·CH(C<sub>6</sub>H<sub>5</sub>)·C(CH<sub>3</sub>)<sub>2</sub>·CO<sub>2</sub>H (*v. infra*); but neither unchanged acid, nor *α*-desylisobutyric acid was observed. The ethereal solution, thus freed from acids, deposited, by spontaneous evaporation, short, flat, six-sided prisms melting at 106° (see preceding experiment). The yield of this substance was 2.8 grams. Recrystallised from alcohol, it exhibited dimorphism. From alcoholic solutions of the impure substance it separated in needles melting at 110°, but from pure solutions in the above form melting at 106°. If a supersaturated solution of the pure substance is seeded with the needles, both forms are deposited. The substance is the *lactone of*

*αα*-dimethyl-*βγ*-diphenyl-*γ*-hydroxybutyric acid,   
(1:1-dimethyl-2:3-diphenylbutyrolactone), and had been formed by the reduction of *α*-desylisobutyric acid, the primary product of the reaction. (See also the synthesis of this lactone described later on.)

Analysis gave figures agreeing with the foregoing formula.

0.1656 gave 0.4924 CO<sub>2</sub> and 0.1013 H<sub>2</sub>O. C = 81.09; H = 6.79.

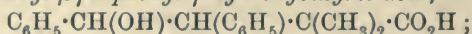
0.1668 „ 0.4962 CO<sub>2</sub> „ 0.1033 H<sub>2</sub>O. C = 81.13; H = 6.88.

C<sub>13</sub>H<sub>18</sub>O<sub>2</sub> requires C = 81.20; H = 6.76 per cent.

In another experiment the alcoholic mother liquor from the foregoing compound deposited eight-sided rectangular laminæ of a neutral substance melting at 145—150°, which we were unable to identify.

Half a gram of this dimethyldiphenylbutyrolactone was warmed on the water-bath with an excess of 5 per cent. alcoholic potassium hydroxide. The mixture set to a thick paste. The substance which remained after expelling the alcohol dissolved without residue in cold water; but, on warming the solution, a crystalline powder separated. After recrystallisation from alcohol, it formed flat prisms melting at 106°. It was identified as *dimethyldiphenylbutyrolactone* by the mixture melting-point test.

The lactone had therefore formed, with alcoholic potash, a soluble salt of *aa-dimethyl-βγ-diphenyl-γ-hydroxybutyric acid*,

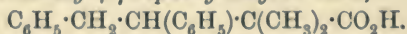


but on warming the aqueous solution, the salt had been hydrolysed and the resulting acid re-lactonised.

*Reduction of α-Desylisobutyric Acid with Sodium in boiling Alcohol: Formation of Dimethyldiphenylbutyrolactone.*—The constitution of the foregoing lactone can be proved by preparing it from *α-desylisobutyric acid* by reduction.

1·3 grams of *α-desylisobutyric acid* were reduced in boiling alcoholic solution with 2·6 grams of sodium. The product was diluted with water, acidified with dilute sulphuric acid, and extracted with ether. Sodium carbonate removed from the ether a small quantity of an acid which crystallised from alcohol in slender needles melting at 142°. (Not identified.) The neutral substance remaining after evaporation of the ether crystallised from ether in the flat prisms of *dimethyldiphenylbutyrolactone* melting at 106°. It was further identified by the mixture melting-point test.

*Reduction of Dimethyldiphenylbutyrolactone with Hydriodic Acid: Formation of aa-Dimethyl-βγ-diphenylbutyric Acid,*



—Seven grams of dimethyldiphenylbutyrolactone (m. p. 106°), 60 grams of hydriodic acid (sp. gr. 1·7), and 2 grams of red phosphorus were heated in a sealed tube at 150° for 5 hours. The product was purified in the ordinary way. An organic acid (yield 0·6 gram), crystallising from alcohol in short prisms melting at 172°, was obtained, whilst 5·4 grams of unchanged substance were recovered.

In the second experiment the mixture was heated to 160—180°. A quarter of the substance was converted into the acid melting at 172°; but the remainder of the product was a thick neutral oil. It is therefore more advantageous to conduct the reduction at 150°.



The acid melting at  $172^{\circ}$  gave figures agreeing with the formula of *aa-dimethyl- $\beta\gamma$ -diphenylbutyric acid*.

0.1654 gave 0.4873  $\text{CO}_2$  and 0.1118  $\text{H}_2\text{O}$ .  $\text{C} = 80.35$ ;  $\text{H} = 7.51$ .

0.1632 „ 0.4811  $\text{CO}_2$  „ 0.1102  $\text{H}_2\text{O}$ .  $\text{C} = 80.39$ ;  $\text{H} = 7.50$ .

$\text{C}_{18}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 80.59$ ;  $\text{H} = 7.46$  per cent.

The silver salt was obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt. The value for silver was found somewhat low.

0.3929 gave 0.1104 Ag.  $\text{Ag} = 28.09$ .

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{Ag}$  requires  $\text{Ag} = 28.78$ .

*Oxidation of aa-Dimethyl- $\beta\gamma$ -diphenyl- $\gamma$ -hydroxybutyric Acid to  $\alpha$ -Desylisobutyric Acid.*—Two grams of dimethyldiphenylbutyrolactone were treated with excess of alcoholic potassium hydroxide and the mixture evaporated to dryness on the water-bath. The residue was dissolved in cold water, and a solution of potassium permanganate was added until the coloration was permanent. The liquid was filtered from the hydrated manganese oxides, acidified, and extracted with ether. Dilute sodium carbonate removed from the ethereal solution 0.4 gram of an acid which crystallised from alcohol in flat needles melting, with decomposition, at  $218^{\circ}$ . These are the properties of  *$\alpha$ -desylisobutyric acid*. The substance was further identified by the mixture melting-point test. A considerable proportion (1.3 gram) of dimethyldiphenylbutyrolactone was recovered unchanged.

On analysis the acid gave figures agreeing with those required for  *$\alpha$ -desylisobutyric acid*.

0.1582 gave 0.4430  $\text{CO}_2$  and 0.0917  $\text{H}_2\text{O}$ .  $\text{C} = 76.37$ ;  $\text{H} = 6.44$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2$  requires  $\text{C} = 76.59$ ;  $\text{H} = 6.38$  per cent.

The foregoing three papers form a continuation of a general investigation of the reactions of ketonic compounds (compare *Trans.*, 1897, 71, 123), and the expenses incidental to the work have for many years past been in great part defrayed by repeated allotments from the Government Grant of the Royal Society.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF ABERDEEN.

### XXX.—*The Estimation of Ethyl Alcohol in Essences and Medicinal Preparations.*

By THOMAS EDWARD THORPE and JOHN HOLMES.

THE estimation of ordinary alcohol in simple mixtures of alcohol and water offers no experimental difficulties. A determination of specific gravity at the standard temperature, and a reference to a table of densities, at once gives the percentage amount of spirit present.

In estimating the amount of spirit in medicinal preparations, such as tinctures of aconite, arnica, belladonna, capsicum, and calumba, these must first be distilled, as the extractive matters present would "obscure" the true percentage of alcohol as shown by the relative density.

On account of the high vapour pressure of ethyl alcohol and its avidity for water, the distillation of a strong spirituous liquid into its own volume so as to obtain an accurate determination of the amount of alcohol present in the liquid becomes practically impossible with the apparatus and the methods of distillation commonly used. It is practicable to distil a strong spirituous liquid into twice its own volume with the requisite degree of accuracy, but distillation into four times the initial volume is perfectly easy, and the results are uniformly accurate to within the degree of accuracy permitted by the spirit tables used, that is to say, if 100 cb.c. of 25 per cent. alcohol are distilled, and the volume of the distillate made up to 100 cb.c., the resulting density will be found not to differ more than 0.00001 from the original density.

The methods above indicated are obviously only applicable to preparations yielding distillates free from essential oils and other volatile substances. Hence such substances must be removed before the spirit can be estimated with any approach to accuracy. Included in this category are ether, chloroform, benzaldehyde, camphor, santal oil, castor oil, ethyl and amyl acetates and butyrates, and the essential oils of lemon, rosemary, juniper, celery, cloves and peppermint.

In such cases the method of treatment in use in the Government Laboratory and which has been found to be of very general applicability is as follows:

25 cb.c. of the sample, measured at 60° F. (15.5° C.), are mixed with water in a separator to a bulk of from 100 to 150 cb.c., and common salt is added in sufficient quantity to saturate the liquid. The mixture is now shaken vigorously for 5 minutes with from 50 to 80

cb.c. of light petroleum, boiling below  $60^{\circ}$  C., and after standing for about half an hour, the lower layer is drawn off into another separator, extracted if necessary a second time with petroleum and then drawn off into a distillation flask. Meanwhile the petroleum layers are washed successively with 25 cb.c. of saturated common salt solution, and the washings added to the main bulk, which is neutralised if necessary, and then distilled and the distillate made up to 100 cb.c.

That the whole of the alcohol which may be present can be recovered by this treatment has been proved by direct experiment with known volumes of spirit of known strength.

It has been found that the alcohol in 25 cb.c. of strong spirit when diluted with water even to the extent of 500 cb.c. and the solution saturated with common salt, can be entirely recovered in the first 100 cb.c. of the distillate.

The results thus obtained require a small correction from the circumstance that, as the alcohol present is distilled into four times its initial volume, the errors of the spirit tables are necessarily quadrupled.

The magnitude of the error can, however, be readily ascertained, once for all, by diluting quantities of 25 cb.c. of spirit of known but of varying strength to 100 cb.c. and determining the sp. gr. of the diluted spirit. There is practically no error due to distillation. The same results are obtained by simple dilution as by distillation into quadruple bulk.

A series of concurrent observations were made in the case of alcoholic mixtures of strengths varying between 160 and 88 per cent. proof spirit, and from the results of these the mean error of the tables at below 40 per cent. proof (say 0.972 sp. gr.), which is the particular section of the tables which is mainly used, may be set down as + 0.2 per cent. of proof spirit, and hence the observed determinations of spirit require a subtractive correction of 0.8 per cent.

The method, as described, is applicable to preparations containing chloroform, ether, benzaldehyde and compound ethers. In the greater number of other cases, for example, essences of lemon, juniper, peppermint and santal oil preparations, it will be found that a single extraction with petroleum is sufficient.

The same method may be applied to distillates which unexpectedly contain oily matter, or which have been obtained intermediately in order to facilitate subsequent extraction, as in the case of *Liq. Picis Carb. B. P.*

In the case of all preparations containing camphor, 25 cb.c. of normal sulphuric acid solution are used instead of common salt, and a single extraction with petroleum is made. Before distilling, it is desirable



to neutralise the sulphuric acid with caustic soda, and if by any chance the volume of the liquid becomes inconveniently large, some common salt is also added. But in preparations containing ammonia this is inadmissible, and the liquid to be distilled must be slightly acid.

This process has been in use in the Government Laboratory for some time past, and many thousands of samples containing a great variety of essential oils and other substances, have been tested by means of it.

The following results obtained on preparations actually made in the laboratory and containing known quantities of ethyl alcohol, are adduced as evidence of the accuracy and general applicability of the method:

| Rectified spirit containing                   | Alcoholic strength of preparation, calculated. |                             | Alcoholic strength found.      |                             |
|---|--|-----------------------------|--------------------------------|-----------------------------|
|   | Volume of alcohol in 100 cb.c.                 | Percentage of proof spirit. | Volume of alcohol in 100 cb.c. | Percentage of proof spirit. |
|   | cb.c.  |                             | cb.c.                          |                             |
| 20 per cent. ethyl acetate .....              | 72·8   | 127·6                       | 72·6                           | 127·3                       |
| 20 " amyl acetate .....                       | 72·4   | 127·0                       | 72·5                           | 127·1                       |
| 30 " ethyl ether, B. P. ....                  | 63·5   | 111·4                       | 63·4                           | 111·1                       |
| 30 " chloroform, B. P. ....                   | 63·5   | 111·4                       | 63·4                           | 111·2                       |
| 10 " camphor, B. P. ....                      | 81·7   | 143·3                       | 81·4                           | 142·7                       |
| 10 " lemon oil .....                          | 81·9   | 143·5                       | 82·1                           | 143·9                       |
| 10 " rosemary oil, B. P. ....                 | 81·6   | 143·0                       | 81·4                           | 142·7                       |
| 10 " benzaldehyde .....                       | 81·9   | 143·6                       | 81·4                           | 142·7                       |
| 10 " santal oil .....                         | 81·2   | 142·3                       | 81·0                           | 142·0                       |
| 10 " peppermint oil, B. P. ....               | 82·0   | 143·8                       | 81·6                           | 143·0                       |
| 5 " juniper oil, B. P. ....                   | 86·4   | 151·5                       | 86·3                           | 151·2                       |
| 20 " fusel oil .....                          | 72·8   | 127·6                       | 72·2                           | 126·5                       |
| <i>Lia. saponis</i> , B. P. ....              | 62·5   | 109·5                       | 62·7                           | 109·9                       |
| <i>Tr. chlor. and morph. co.</i> , B. P. .... | 55·5   | 97·3                        | 55·5                           | 97·2                        |
| <i>Lia. sinapis</i> , B. P. ....              | 66·8   | 117·1                       | 66·9                           | 117·3                       |
| <i>Liq. picis. carb.</i> , B. P. ....         | 82·4   | 144·4                       | 82·2                           | 144·0                       |

As evidence of the degree of variation which may be expected to occur between the results of different operators we append the following results:

*Results of Different Operators.*

|   | A.                             |                             | B.                             |                             | C.                             |                             | D.                             |                             | Alcoholic strength of preparation, calculated. |
|---|--------------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|--|
|   | Volume of alcohol in 100 cb.c. | Percentage of proof spirit. | Volume of alcohol in 100 cb.c. | Percentage of proof spirit. | Volume of alcohol in 100 cb.c. | Percentage of proof spirit. | Volume of alcohol in 100 cb.c. | Percentage of proof spirit. |  |
| Spirits of chloroform (33 per cent.) .....    | cb.c.<br>60.0                  | 105.1                       | cb.c.<br>60.1                  | 105.4                       | cb.c.<br>59.9                  | 105.0                       | cb.c.<br>—                     | —                           | 105.3  |
| Spirits of ether (33 per cent.) .....         | 59.9                           | 105.0                       | 60.1                           | 105.3                       | 59.8                           | 104.9                       | 60.0                           | 105.2                       | 105.3  |
| Spirits of camphor (10 per cent.) .....       | 81.1                           | 142.2                       | 81.0                           | 142.0                       | 81.2                           | 142.3                       | —                              | —                           | 142.7  |
| <i>Līm. saponis</i> .....                     | 62.9                           | 110.2                       | 62.8                           | 110.1                       | 63.2                           | 110.7                       | 63.4                           | 111.0                       | 111.1  |
| <i>Tr. chlor. and morph. Co.</i>              | 49.9                           | 87.4                        | 49.5                           | 86.8                        | 49.8                           | 87.2                        | —                              | —                           | 87.3   |
| Essence of lemon .....                        | 73.2                           | 128.3                       | 73.2                           | 128.4                       | 73.4                           | 128.7                       | —                              | —                           | 128.2  |
| Ethyl acetate in alcohol (20 per cent.) ..... | 72.7                           | 127.5                       | 73.5                           | 128.9                       | 72.7                           | 127.5                       | —                              | —                           | 128.1  |
| Fusel oil in alcohol (20 per cent.) .....     | 72.2                           | 126.6                       | 71.9                           | 126.0                       | 72.5                           | 127.0                       | —                              | —                           | 127.7  |

### XXXI.—*Carbon Monoxide as a Product of Combustion by the Bunsen Burner.*

By THOMAS EDWARD THORPE.

IN the course of an inquiry into the nature of the combustion-products of certain of the gas and oil-stoves in common use, made at the instance of the Factory Inspection Department of the Home Office, I have had an opportunity of making some observations on the behaviour of the Bunsen burner as regards its liability to evolve unburnt carbon monoxide when burning under ordinary conditions. That considerable quantities of carbon monoxide may escape unburnt when a coal-gas flame impinges upon a cooled surface is proved by the many fatal instances of carbonic oxide poisoning which have occurred as the result of burning such gas in the so-called "geysers" or underneath baths placed in small and ill-ventilated rooms. Professor Vivian Lewes, some years ago, showed (Cantor Lectures on Gaseous Illuminants: *J. Soc. Arts*, 1891), that when the flame of a Bunsen burner was placed beneath a copper vessel containing water in such a manner that the inner cone of the flame impinged, or apparently impinged, upon the metal, carbon monoxide could be detected among the escaping products of combustion.

My experiments were made with a view of determining how much carbonic oxide escaped when the flame of a Bunsen lamp was caused to burn beneath a sand-tray in the manner required, say, to heat a wash bottle. The lamp and tray were placed under a cover provided with adequate inlets and outlets for air, and the relation of the carbon dioxide to the carbon monoxide formed was ascertained by aspirating known volumes of the air from within the cover through an apparatus which allowed of their simultaneous determination.

The amount of carbon dioxide was ascertained by absorption by means of soda-lime; that of the carbon monoxide by the very convenient method of Nicloux and Gautier, as modified by Kinnicut and Sanford (*J. Amer. Chem. Soc.*, 1900, 22, 14). This method is based on the observation of Ditte that at temperatures between 150° and 200°, iodine pentoxide is decomposed by carbon monoxide in accordance with the equation :



the liberated iodine being determined by means of N/1000 solution of sodium thiosulphate. Kinnicut and Sanford have shown that this method is far more sensitive than any modification of Hoppe-Seyler's method based on the difference of the spectroscopic reactions,



under the influence of reducing agents, of carbon monoxyhaemoglobin and oxyhaemoglobin, and that with suitable precautions it is capable of yielding accurate quantitative results even in the case of air containing as little as 0·0025 per cent. by volume. It has been tested in the Government Laboratory, and the statements as to its accuracy have been confirmed.

Known quantities of carbon monoxide were mixed with air, and the mixture slowly aspirated over the iodine pentoxide heated at 150—155°, and the liberated iodine absorbed in a 10 per cent. solution of potassium iodide, and the amount determined by N/1000 sodium thiosulphate solution with the following results :

| Percentage vol. of<br>carbon monoxide in air. | Found. |
|---|--------|
| 0·190   | 0·197  |
| 0·148   | 0·146  |
| 0·062   | 0·061  |

In an actual experiment with the Bunsen lamp burning under the sand-tray, 10 litres of air mixed with some portion of the products of combustion of gas, burning under a pressure of 0·95 inches and at the rate of 6 cubic feet per hour, were aspirated through the apparatus : the weight of carbon dioxide absorbed was 0·175 gram, or 0·8906 per cent. by volume. The iodine liberated by the carbon monoxide required 11·9 c.c. (corr.) of the sodium thiosulphate solution, this amount being equivalent to 0·0066 per cent. of carbon monoxide by volume.

Hence if the coal gas is assumed to yield one half of its volume of carbon dioxide when completely burned, it would appear from the ratio 0·0066/0·8906, that as much as 0·022 of a cubic foot of carbon monoxide per hour escapes unburnt from a Bunsen burner when used in the circumstances described.

It should be stated that care was taken to exclude the possible disturbing influence of any unsaturated hydrocarbons among the products of combustion by treatment of the gases with strong sulphuric acid containing sulphuric anhydride, and that a control experiment was made by aspirating a known volume of the air of the laboratory through the apparatus and deducting the volume of thiosulphate needed to decolorise the minute amount of iodine so liberated from the volume of the thiosulphate actually consumed in determining the amount of carbon monoxide produced by the Bunsen burner.

GOVERNMENT LABORATORY,  
LONDON.

# XXXII.—*Synthesis of Iminoethers. N-Ethyl, N-Methyl, and N-Benzyl Benziminoethers.*

By G. DRUCE LANDER, D.Sc.

AMONGST the open chain nitrogen substituted iminoethers of the type  $R_1C(OR_{11})NR_{11}$  we are at present acquainted only with those in which  $R_{11}$  is an aryl group. It seemed therefore of interest to undertake the preparation of the *N*-alkyl and benzyliminoethers. Benziminoethers of this class are described in the present paper.

Of the methods available for their formation from the acylated amines (Trans., 1901, 79, 690 ; and 1902, 81, 591) that of alkylation by means of dry silver oxide and alkyl iodides has proved of no practical value. In a test experiment, 7.5 grams of benzethylamide after boiling for 3 hours with 23 grams of dry silver oxide and 32 grams of ethyl iodide gave only 0.5 gram of *N*-ethylbenziminoethyl ether. The failure of the reaction is doubtless attributable to the diminished acidity of the substituted amide caused by the introduction of the relatively basic alkyl group. Recourse had therefore to be taken to the method of synthesis from the imide chlorides by the action of sodium alkyloxides, a process which leads to the formation of the desired products, in a manner generally similar to that previously described for the aryl benzamides.

## EXPERIMENTAL.

### I. *N*-Ethylbenziminoethers.

The imide chloride of benzethylamide,  $Ph \cdot CCl : N Et$ , has not previously been described. It is formed similarly to the methyl analogue (Pechmann, *Ber.*, 1895, 28, 2367) by the interaction of phosphorus pentachloride and benzethylamide in molecular proportion. After distilling off the phosphorus oxychloride under diminished pressure, the imide chloride boils at 110—111° under 15 mm. pressure, forming a colourless limpid liquid. The first portions of the distillate contain a solid (compare Pechmann, *loc. cit.*), which subsequently volatilises out of the warm distillate.

The imide chloride was not analysed, its identity being established by the following reactions: the regeneration of benzethylamide by the action of water, the formation of iminoethers through the agency of sodium alkyloxides, and the production of *phenylethylbenzenylamidine* by condensation with aniline. When aniline was added to a solution of the imide chloride in light petroleum, the hydrochloride of this

amidine was deposited as a sticky mass, which was extracted with dilute sulphuric acid. On adding potassium iodide the hydriodide of the amidine was precipitated as a brown resin from which the base was obtained by decomposition with sodium carbonate. After two crystallisations from dilute alcohol it formed small colourless needles (m. p. 74—76°).

The platinichloride is sparingly soluble in water and is deposited from dilute alcohol in yellow prisms which decompose at 204°.

0.5486 lost 0.0221 at 100° and gave 0.1200 Pt.  $H_2O = 4.02$  ;  
Pt = 22.8.

$(Ph \cdot C : N Et \cdot N H Ph)_2 \cdot H_2PtCl_6 \cdot 2H_2O$  requires  $H_2O = 4.03$  ; Pt (in the dry salt) 22.71 per cent.

The work of Pechmann on mixed amidines (*loc. cit.*) leaves no doubt that the constitution of the above base is expressed by the formula  $Ph \cdot C(:NEt) \cdot N H Ph$  and not  $Ph \cdot C(:N Ph) \cdot N H Et$ .

*N-Ethylbenziminioethyl ether*,  $Ph \cdot C(OEt) : N Et$ , constitutes the main product of the action of sodium ethoxide on a light petroleum solution of the imide chloride. Benzoyl diethylbenzenylamidine (Trans., 1902, 81, 594), isolated in the preparation of the methyl-iminoether, is doubtless also formed. The iminoether is, however, contaminated with some unrecognised impurity. In one case, the imide chloride was separated by distillation under diminished pressure into two fractions boiling at 118—124° and 124—125° respectively, and these, freed as far as possible from solid (see above) by solution in light petroleum, were separately treated with an alcoholic solution of sodium ethoxide, and the resulting iminoether isolated by distillation under diminished pressure in a manner similar to that formerly employed. In each instance, the iminoether distilled between 105° and 115° under 15 mm. pressure, and each of the two products was then divided into three fractions by distillation at the ordinary pressure, the total yield of distilled product from 30 grams of benzethylamide being 17 grams. The extreme boiling points were 215° and 227°, and repeated analysis showed that none of the fractions was pure. Fractions boiling at 218—221° and 223—227° gave  $C = 73.56$ ,  $H = 8.54$ , and  $C = 71.3$ ,  $H = 8.3$  respectively, the formula  $C_{11}H_{15}ON$  requiring  $C = 74.57$ ,  $H = 8.47$  per cent.

Boiling point and composition alike indicated that a liquid of higher boiling point and smaller carbon content than the iminoether was probably present. Fractionation with the comparatively small quantity of substance available did not lead to a separation. It seemed, however, not unlikely that the impurity might be a compound of the formula  $Ph \cdot C(OEt)_2 \cdot N H Et$ . Open chain mixed ortho-compounds of this type have not been hitherto obtained. I have, however, recently



prepared such derivatives corresponding with the oxanilic esters, the formation and properties of which I hope soon to be able to communicate. It might be supposed that an ortho-compound of the type indicated would readily lose alcohol on heating, giving an iminoether; that this is not necessarily the case is shown by the oxalic compounds above referred to.\* And although the compound  $\text{Ph}\cdot\text{C}(\text{OEt})_2\cdot\text{NHEt}$  is more likely to lose alcohol on distillation (compare p. 325), it is still possible that the change might not be complete. The elimination of alcohol would probably be facilitated by warming with a dehydrating agent, and acetic anhydride, which does not appear to react with this class of nitrogen substituted iminoethers, seemed to be the most suitable.

Impure *N*-ethylbenziminoethyl ether (9.5 grams) boiling at 219—226° was mixed with 0.6 gram of acetic anhydride and warmed in an oil-bath. At about 160°, the liquid began to boil and the odour of ethyl acetate was distinctly perceptible. The warming was continued for a few minutes and, after cooling, moderately concentrated potassium hydroxide solution was added.

The iminoether was extracted with ether, dried with calcium chloride, and distilled under 12 mm. pressure, when two fractions 106—107° and 107—109° were obtained. The second fraction was analysed:

0.1334 gave 0.3636  $\text{CO}_2$  and 0.1015  $\text{H}_2\text{O}$ .  $\text{C} = 74.33$ ;  $\text{H} = 8.45$ .

$\text{C}_{11}\text{H}_{15}\text{ON}$  requires  $\text{C} = 74.57$ ;  $\text{H} = 8.47$  per cent.

The purified compound, which was analysed after distillation, boiled at 221—223° (uncorr.) under the ordinary pressure:

0.1339 gave 0.3650  $\text{CO}_2$  and 0.1020  $\text{H}_2\text{O}$ .  $\text{C} = 74.34$ ;  $\text{H} = 8.46$ .

A second treatment with 1/10 molecular proportion of acetic anhydride yielded a product boiling at 105° under 11 mm. pressure, and giving  $\text{C} = 74.31$ ,  $\text{H} = 8.59$ . Nitrogen was determined in this specimen:

0.1300 gave 9.0 c.c. moist nitrogen at 13° and 750 mm.  $\text{N} = 8.05$ .

$\text{C}_{11}\text{H}_{15}\text{ON}$  requires  $\text{N} = 7.9$  per cent.

*N*-Ethylbenziminoethyl ether is a limpid, colourless liquid, with a pungent odour recalling that of the alkylamines. Anhydrous hydrogen chloride precipitates an oily hydrochloride from petroleum solution, which yields ethyl chloride and benzethylamide on heating. Aqueous hydrochloric acid brings about the usual resolution into ethyl benzoate and amine.

\* The compound  $\text{CO}_2\text{Me}\cdot\text{C}(\text{OMe})_2\cdot\text{NHPh}$ , for example, distils unchanged in a vacuum, and, on heating under the ordinary pressure, undergoes profound decomposition.

By warming with aniline at  $100^{\circ}$  for 3 hours, phenylethylbenzenylamidine (m. p.  $74-76^{\circ}$ ) is produced, the product being identical in all respects with that prepared from the imide chloride.

*N-Ethylbenziminomethyl ether*,  $\text{Ph}\cdot\text{C}(\text{OMe})\cdot\text{NEt}$ .—Thirty grams of imide chloride were obtained from 30 grams of benzethylamide and 42 grams of phosphorus pentachloride and this product, which required 3.8 grams of sodium dissolved in methyl alcohol, gave 20 grams of crude *N*-ethylbenziminomethyl ether. After treatment with acetic anhydride (0.1 mol.) the iminoether distilled between  $97^{\circ}$  and  $100^{\circ}$  under 11 mm. pressure:

0.1186 gave 0.3180  $\text{CO}_2$  and 0.0875  $\text{H}_2\text{O}$ .  $\text{C} = 73.12$ ;  $\text{H} = 8.19$ .

$\text{C}_{10}\text{H}_{13}\text{ON}$  requires  $\text{C} = 73.62$ ;  $\text{H} = 7.97$  per cent.

A specimen, purified by repeating this treatment, was also analysed:

0.1240 gave 0.3330  $\text{CO}_2$  and 0.0891  $\text{H}_2\text{O}$ .  $\text{C} = 73.23$ ;  $\text{H} = 7.98$ .

The boiling point under the ordinary pressure is  $209-212^{\circ}$  (uncorr.).

*Benzoyldiethylbenzenylamidine*,  $\text{Ph}\cdot\text{C}(\text{:NEt})\cdot\text{NEt}\cdot\text{COPh}$ , was slowly deposited from a chloroform solution of the yellow gummy residue left after distillation of the crude iminoether; it separates in dense, colourless prisms, which, after two crystallisations from chloroform and ether, melt without decomposition at  $90-91.5^{\circ}$ :

0.1435 gave 0.4052  $\text{CO}_2$  and 0.0946  $\text{H}_2\text{O}$ .  $\text{C} = 77.01$ ;  $\text{H} = 7.32$ .

0.1472 „ 0.4175  $\text{CO}_2$  „ 0.0965  $\text{H}_2\text{O}$ .  $\text{C} = 77.33$ ;  $\text{H} = 7.21$ .

$\text{C}_{15}\text{H}_{20}\text{ON}_2$  requires  $\text{C} = 77.14$ ;  $\text{H} = 7.14$  per cent.

This compound is a base, in which respect it differs from the benzoylated arylbenzenylamidines which are neutral bodies, and resembles benzoylbenzamidine (Eitner, *Ber.*, 1892, 25, 467). It is readily soluble in cold dilute hydrochloric acid and is reprecipitated unchanged by alkalis: The *platinichloride*, which is precipitated in minute orange prisms when platinic chloride is added to a solution of the base in hydrochloric acid, is anhydrous, and decomposes at  $151-151.5^{\circ}$ .

0.3672 gave 0.0746 Pt.  $\text{Pt} = 20.3$ .

$\{\text{Ph}\cdot\text{C}(\text{:NEt})\cdot\text{NEt}\cdot\text{COPh}\}_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 20.1$  per cent.

On prolonged standing, and more rapidly on warming, the solution of the benzoylated amidine in hydrochloric acid undergoes decomposition. Benzoic acid and ethylamine could be detected, and a neutral compound, melting at  $101-102^{\circ}$  after crystallisation from dilute alcohol, was also formed, but in quantity insufficient for analysis.

II. *N-Methylbenziminoothers.*

*N-Methylbenziminomethyl ether*,  $\text{Ph}\cdot\text{C}(\text{OMe})\cdot\text{NMe}$ .—The imide chloride of benzmethylanide has been described by Pechmann (*loc. cit.*), who failed to obtain it in a state of purity, and regarded it as contaminated with an impurity of higher boiling point, which is free from chlorine.

For the preparation of the iminoether, the imide chloride may first be distilled, or the residue left after removal of phosphorus oxychloride from the product of reaction of the pentachloride with benzmethylanide may be dissolved in benzene and treated with sodium methoxide in alcoholic solution. In either case an impure iminoether results, with benzoyldimethylbenzenylamidine as a by-product.

The boiling point and analytical data of the iminoether were similar to those of *N*-ethylbenziminooethyl ether, indicating the presence of a similar impurity, and treatment with acetic anhydride was found to effect the required purification. After warming twice with acetic anhydride (0.1 mol.) the iminoether was obtained in a pure state and distilled almost completely at  $94\text{--}95^\circ$  under 12 mm., and at  $203\text{--}206^\circ$  (uncorr.) under the atmospheric pressure :

0.1274 gave 0.3380  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ .  $\text{C} = 72.35$ ;  $\text{H} = 7.55$ .

0.1116 „ 0.2958  $\text{CO}_2$  „ 0.0750  $\text{H}_2\text{O}$ .  $\text{C} = 72.28$ ;  $\text{H} = 7.46$ .

$\text{C}_9\text{H}_{11}\text{ON}$  requires  $\text{C} = 72.48$ ;  $\text{H} = 7.38$  per cent.

The compound is a colourless, limpid liquid of amine-like odour. Ethereal hydrogen chloride gave an impure hydrochloride, melting at  $65\text{--}70^\circ$ , with evolution of methyl chloride and regeneration of benzmethylanide.

On warming some of the iminoether with aniline at  $100^\circ$  for 6 hours, phenylmethylbenzenylamidine melting at  $132\text{--}134^\circ$  was formed (compare Pechmann, *loc. cit.*).

*Benzoyldimethylbenzenylamidine*,  $\text{Ph}\cdot\text{C}(\text{NMe})\cdot\text{NMe}\cdot\text{COPh}$ , was isolated from the product of reaction of the imide chloride with sodium methoxide, in the manner already described; after crystallisation from chloroform and light petroleum, it formed colourless prismatic crystals melting at  $116\text{--}117.5^\circ$  :

0.1360 gave 0.3796  $\text{CO}_2$  and 0.0804  $\text{H}_2\text{O}$ .  $\text{C} = 76.12$ ;  $\text{H} = 6.56$ .

0.1220 „ 11.8 c.c. moist nitrogen at  $15^\circ$  and 758 mm.  $\text{N} = 11.27$ .

$\text{C}_{16}\text{H}_{16}\text{ON}_2$  requires  $\text{C} = 76.19$ ;  $\text{H} = 6.35$ ;  $\text{N} = 11.11$  per cent.

Like its ethyl analogue, this compound is a base. The platinumchloride forms anhydrous, orange-coloured prisms decomposing at  $184\text{--}185^\circ$  :

0.5256 gave 0.1124 Pt.  $\text{Pt} = 21.38$ .

$(\text{C}_{16}\text{H}_{16}\text{ON}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 21.31$  per cent.



On warming with dilute hydrochloric acid, the base yields methylamine, benzoic acid, and a neutral solid melting at 91—95° which has not yet been examined.

*Attempt to Prepare the Ortho-compound,  $\text{Ph}\cdot\text{C}(\text{OMe})_2\cdot\text{NHMe}$ .—* When molecular proportions of phosphorus pentachloride and benzmethylamide are mixed in the cold, and care is taken to avoid overheating, a slight rise of temperature is observed, and the mass melts without evolution of hydrogen chloride. On cooling, the brown syrup becomes filled with needle-shaped crystals, which almost certainly consist of the amide chloride,  $\text{Ph}\cdot\text{CCl}_2\cdot\text{NHMe}$ , but the substance liquefies on exposure for a few seconds to moist air, so that neither the melting point nor the composition could be determined. On warming, the imide chloride is formed in the usual manner, but I am inclined to regard it as at least possible that a small proportion of the amide chloride distils over unchanged with the imide chloride, which would account for the composition of the iminoether and its behaviour towards acetic anhydride. This supposition would be capable of verification if the amide chloride could be isolated and made to react with sodium methoxide in accordance with the equation:  $\text{Ph}\cdot\text{CCl}_2\cdot\text{NHMe} + 2\text{NaOMe} = \text{Ph}\cdot\text{C}(\text{OMe})_2\cdot\text{NHMe} + 2\text{NaCl}$ .

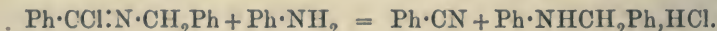
The solid, supposed amide chloride, from 8.5 grams of benzmethylamide was separated by dissolving the product of reaction in dry benzene, precipitating with light petroleum, and drying for an hour in an exhausted desiccator; it was then redissolved in benzene and treated with a methyl-alcoholic solution of sodium methoxide. On distillation in a vacuum the chief fraction, which boiled at 86—88° under 11 mm. pressure, weighed 1.3 grams and gave  $\text{C} = 70.92$ ;  $\text{H} = 7.42$ ,  $\text{C}_9\text{H}_{11}\text{ON}$  requiring  $\text{C} = 72.48$ ;  $\text{H} = 7.4$  and  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$  requiring  $\text{C} = 66.2$ ;  $\text{H} = 8.3$  per cent. The composition of the product differs so little from that of the iminoether, prepared from distilled imide chloride, that no certain conclusions can be drawn regarding its probable constitution.

*N-Methylbenziminioethyl ether,  $\text{Ph}\cdot\text{C}(\text{OEt})\cdot\text{NMe}$ ,* was not obtained in a pure state owing to lack of material. The boiling point of the crude compound lay between 103—108° under 14 mm., and 214—217° under the ordinary pressure. The percentage composition of the small amount which distilled at 215° was  $\text{C} = 72.2$ ;  $\text{H} = 8.0$ ;  $\text{N} = 7.9$ ; the calculated values being  $\text{C} = 73.6$ ;  $\text{H} = 7.97$ ;  $\text{N} = 8.6$  per cent.

The properties of the substance, however, left no doubt that the iminoether formed the major part of the product.

III. *N*-Benzylbenziminooethers.

The imide chloride of benzbenzylamide,  $\text{Ph}\cdot\text{CCl}\cdot\text{NCH}_2\text{Ph}$ , has been described by Pechmann and Heinze (*Ber.*, 1897, 30, 1788) who assigned to it the boiling point  $110^\circ$  under 80 mm. pressure. According to these authors, this imide chloride is decomposed by aniline or methylaniline into benzonitrile and benzylaniline or benzylmethylaniline, thus:



This anomalous behaviour proves, however, to be due to the instability of the imide chloride, which, on attempted distillation, splits almost completely into a mixture of benzonitrile and benzylchloride  $\text{Ph}\cdot\text{CCl}\cdot\text{NCH}_2\text{Ph} = \text{Ph}\cdot\text{CN} + \text{CH}_2\text{PhCl}$ ; at the same time a certain amount of the imide chloride passes over unchanged.\* This is shown by a comparison of the results of iminoether synthesis with distilled and undistilled imide chloride respectively. Moreover, if the imide chloride is not distilled, the synthesis of the mixed phenylbenzylbenzenylamidine of Beckmann and Fellrath (*Annalen*, 1893, 273, 1) can be effected in the usual way.

*Distillation of the Imide Chloride of Benzbenzylamide and Action of Sodium Ethoxide on the Distillate.*—Ten grams each of phosphorus pentachloride and benzbenzylamide were mixed and made to react by gentle warming. After removing phosphorus oxychloride in a vacuum below  $45^\circ$ , the temperature of the bath was raised. With the bath at  $180^\circ$ , distillation began at  $80^\circ$  under 12 mm. pressure, and continued slowly, the temperature steadily rising until the distillation thermometer indicated  $160^\circ$ , the pressure throughout remaining constant. At this temperature the flask became filled with white fumes, and the operation was stopped. The distillate, a pale yellow, mobile liquid, represented about one-half of the reaction mixture; the residue was dark brown and tarry, and gave, on extraction with dilute sulphuric acid, a base which formed an insoluble hydriodide, and was probably an amidine, a considerable quantity of benzbenzylamide remaining undissolved. The results of a second experiment confirmed these observations.

The distillate, which gave a slightly turbid solution in light petroleum, was rendered distinctly alkaline by the addition of a solution of about 0.3 gram of sodium in ethyl alcohol. After washing with water and desiccation with potassium carbonate it was distilled, when the greater part passed over between  $100\text{--}105^\circ$  under 30—40 mm. pressure.

\* A similar observation, made by Ley and Holzweissig, was published (*Ber.*, 1903, 36, 19) after this paper had been handed in for publication.

The distillation then stopped and the second fraction boiling at  $185^{\circ}$  under 9 mm. pressure, was shown by its behaviour towards aqueous hydrochloric acid to be *N*-benzylbenziminooethyl ether (described later). The amount formed was small, but served to show that some imide chloride had distilled unchanged. The lower boiling fraction was re-distilled between  $183$ — $187^{\circ}$  under the ordinary pressure, and on boiling for 6 hours with concentrated aqueous potassium hydroxide gave ammonia and benzoic acid, thus proving the presence of benzonitrile, and a neutral oil free from nitrogen and halogen, boiling at  $183^{\circ}$  (uncorr.) and possessing the characteristic odour of the benzyl alkyl ethers. The formation of benzyl ethyl ether points to the presence of benzyl chloride in the distillate.

*Synthesis of Phenylbenzylbenzenylamidine*,  $\text{Ph}\cdot\text{C}(\text{:NCH}_2\text{Ph})\cdot\text{NHPh}$ , from the Imide Chloride of Benzbenzylamide.—After distilling phosphorus oxychloride under diminished pressure from the reaction product of equal weights of phosphorus pentachloride and benzbenzylamide, the syrupy residue was dissolved in light petroleum and one mol. of aniline was added. After some time, the petroleum was poured off and was found to contain no benzonitrile. The residual hydrochloride was extracted with dilute sulphuric acid, and the amidine liberated by adding sodium hydroxide. After two crystallisations from dilute alcohol the base melted at  $99$ — $100^{\circ}$  and proved to be identical with Beckmann and Fellrath's product from the imide chloride of benzphenylamide and benzylamine (*loc. cit.*).

0.1403 gave 0.4322  $\text{CO}_2$  and 0.0815  $\text{H}_2\text{O}$ .  $\text{C} = 84.01$ ;  $\text{H} = 6.45$ .

$\text{C}_{20}\text{H}_{18}\text{N}_2$  requires  $\text{C} = 83.9$ ;  $\text{H} = 6.3$  per cent.

*Phenylmethylbenzylbenzenylamidine*,  $\text{Ph}\cdot\text{C}(\text{:NCH}_2\text{Ph})\cdot\text{NMePh}$ , was prepared by adding methylaniline (1 mol.) dissolved in benzene to a solution of the undistilled imide chloride of benzbenzylamide in the same solvent. A clear brown solution of the hydrochloride was thus obtained from which the base was separated by distilling off the solvent, extracting the residue with dilute sulphuric acid, and precipitating the clear solution with alkali. After three crystallisations, the base was obtained in colourless prisms melting constantly at  $89$ — $90^{\circ}$ , and not  $95^{\circ}$  as given by Pechmann and Heinze (*loc. cit.*):

0.1164 gave 0.3578  $\text{CO}_2$  and 0.0706  $\text{H}_2\text{O}$ .  $\text{C} = 83.83$ ;  $\text{H} = 6.73$ .

$\text{C}_{21}\text{H}_{20}\text{N}_2$  requires  $\text{C} = 84.0$ ;  $\text{H} = 6.66$  per cent.

This compound was also formed when the synthetic amidine, the formation of which has just been described, was methylated by boiling for 2—3 hours with excess of methyl iodide; when liberated from its hydriodide and crystallised from dilute alcohol, it melted at  $89$ — $90^{\circ}$ , and did not depress the melting point of the preceding preparation



The correctness of the formula  $\text{Ph}\cdot\text{C}(\text{:NCH}_2\text{Ph})\cdot\text{NHPh}$ , proposed by Pechmann for Beckmann and Fellrath's amidine, is thus confirmed.

*N-Benzylbenziminioethyl ether*,  $\text{Ph}\cdot\text{C}(\text{OEt})\text{:NCH}_2\text{Ph}$ , was prepared by mixing an alcoholic solution of sodium ethoxide and a light petroleum solution of the undistilled imide chloride in the same way as that previously described (Trans., 1902, 81, 593). On distilling the product under diminished pressure, the ether was obtained as a thick, colourless, odourless oil boiling at 186—188° under 12 mm. pressure :

0.1430 gave 0.4200  $\text{CO}_2$  and 0.0934  $\text{H}_2\text{O}$ .  $\text{C}=80.1$  ;  $\text{H}=7.25$ .

0.1850 ,, 9.2 c.c. moist nitrogen at 12° and 766 mm.  $\text{N}=5.93$ .

$\text{C}_{16}\text{H}_{17}\text{ON}$  requires  $\text{C}=80.3$  ;  $\text{H}=7.1$  ;  $\text{N}=5.85$  per cent.

The iminoether, which did not give a solid hydrochloride, was hydrolysed by aqueous mineral acids into ethyl benzoate and benzylamine, and, on condensation with aniline, gave Beckmann and Fellrath's amidine.

*N-Benzylbenziminomethyl ether*,  $\text{Ph}\cdot\text{C}(\text{OMe})\text{:NCH}_2\text{Ph}$ , prepared like the ethyl compound, boiled at 178—180° under 11 mm. pressure, 19 grams of purified product being formed from 30 grams benzbenzylamide :

0.2086 gave 11.0 c.c. moist nitrogen at 15° and 752 mm.  $\text{N}=6.1$ .

$\text{C}_{15}\text{H}_{15}\text{ON}$  requires  $\text{N}=6.2$  per cent.

The properties of the methyl compound resemble those of the ethyl homologue, and it gives the amidine melting at 99—100° on condensation with aniline.

*The Oxidation of the N-Benzylbenziminio Ethers by Atmospheric Oxygen.*—The *N*-benzylbenziminio ethers are sharply distinguished from the allied aryl- and alkyl-compounds by the ease with which they are oxidised on exposure to air. In a few days, the liquid iminoethers deposit long, prismatic crystals which, after crystallisation from dilute alcohol, melt at 147—148°. The solid is soluble in cold potassium hydroxide, and is recovered unchanged by immediate acidification. After a time, the alkaline solution deposits leaflets of benzamide melting at 125°.

This behaviour and the analytical data leave no doubt that the solid is dibenzamide (m. p. 148°).

0.1344 gave 0.3685  $\text{CO}_2$  and 0.0612  $\text{H}_2\text{O}$ .  $\text{C}=74.8$  ;  $\text{H}=5.1$ .

0.1573 gave 8.9 c.c. moist nitrogen at 19° and 755 mm.  $\text{N}=6.4$ .

$\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{C}=74.7$  ;  $\text{H}=4.9$  ;  $\text{N}=6.2$  per cent.

The mechanism of the oxidation of the compounds  $\text{PhCOR}\text{:NCH}_2\text{Ph}$  to  $\text{PhCO}\cdot\text{NH}\cdot\text{COPh}$  cannot readily be explained in a satisfactory manner, and in consequence of the hydrolysis of the iminoethers by

acids and of dibenzamide by alkalis, it is not easy to find an alternative oxidising agent. Hydrogen peroxide and neutralised Caro's acid are apparently not suitable, and slightly alkaline potassium ferricyanide gives mainly unaltered iminoether and potassium benzoate.

Much of the expense of the above work was defrayed by a grant made by the Research Fund Committee of the Chemical Society, for which I desire to express my indebtedness.

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NOTTINGHAM.

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### XXXIII.—*Tertiary Butylphenol.*

By EDWARD W. LEWIS (Salters' Research Fellow).

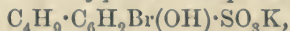
IN studying the action of bromine on the alkyl derivatives of phenol-*p*-sulphonic acid, in order to determine the degree in which the inhibiting influence of the alkyl is dependent on the character of the radicle (Armstrong and Lewis, Proc., 1900, 16, 157), experiments were made with what at the time was supposed to be *ter*.-butylphenyl ether sulphonate; but as the effect produced by the tertiary radicle seemed to be altogether different, not only from that of methyl and ethyl, but also from that of normal and *isobutyl*, the experiments were continued. The object of this note is to point out that the interpretation to be put upon the results is entirely different from that which at the time seemed to be the natural one.

Finding that the phenol-*p*-sulphonate could not be alkylated by the method successfully adopted in all other cases by digesting the salt with *ter*.-butyl chloride in presence of alkali, in order to prepare the ether, a mixture of phenol with the chloride and excess of alkali, together with sufficient alcohol to make a clear solution, was digested until interaction was complete; much gas (butylene) was given off during the operation. To isolate the product, the oil which separated on pouring the strongly alkaline alcoholic solution into water was distilled in a current of steam; the oil thus obtained was assumed to be the required ether and therefore a portion was at once sulphonated. The potassium salt of the acid so produced—which gave correct values on analysis—rapidly absorbed a molecular proportion of bromine, but the sulphonic group was not displaced, a monobromosulphonate being apparently the only product. This result was confirmed by a repetition of the experiments and by a determination of the acidity of the solution after bromination.

Suspicion was first aroused when a small quantity of the oil which escaped sulphonation was identified with *ter*.-butylphenol; it then appeared probable either that the supposed ether was in reality butylphenol or that the ether or a part of it underwent isomeric change under the action of the sulphonating agent (monochlorhydrin). On further brominating the monobromosulphonate, a product was obtained possessing the properties of a phenol, not those of an ether, so that there could be no doubt that butylphenolsulphonic acid and not *ter*.-butylphenyl ethersulphonic acid had been formed. In order to decide between the two alternatives, a considerable quantity of phenol (150 grams) was butylated as before. On subjecting the steam distillate to a rigorous washing with caustic soda solution of moderate strength, the greater part of the oil dissolved in the alkali; the insoluble portion amounted to only about 5 grams, boiling between 190° and 210°. This latter, however, as well as the soluble part, gave only butylphenolsulphonic acid on sulphonation; so that if the oil insoluble in alkali were indeed the ether, it had undergone isomeric change during sulphonation. Experiments made subsequently showed that no such change occurs in the case of *isobutylphenyl* ether, for on sulphonating this substance the sulphonic acid of *isobutylphenyl* ether was alone obtained.

The following new derivatives of *ter*.-butylphenol have been obtained in the course of the experiments.

*Potassium-2-bromo-4-ter.-butylphenol-6-sulphonate*,



obtained by the action of a molecular proportion of bromine on an aqueous solution of potassium *ter*.-butylphenolsulphonate, crystallises from water in anhydrous, glistening, flattened needles or thin flakes:

0.0981 gave 0.0247  $\text{K}_2\text{SO}_4$ .  $\text{K} = 11.29$ .

0.0978 „ 0.0532 AgBr.  $\text{Br} = 23.15$ .

$\text{C}_{10}\text{H}_{12}\text{OBr}\cdot\text{SO}_3\text{K}$  requires  $\text{K} = 11.24$ ;  $\text{Br} = 23.05$ .

*2:6-Dibromo-ter.-butylphenol*, obtained by the further action of bromine on an aqueous solution of the bromosulphonate just described, crystallises in colourless, glistening flakes which melt at 70—71°; it has a faint but rather pleasant odour recalling that of artificial musk:

0.1179 gave 0.1438 AgBr.  $\text{Br} = 51.70$ .

$\text{C}_{10}\text{H}_{12}\text{OBr}_2$  requires  $\text{Br} = 51.95$ .

It is evident from the above observations that the principal product of the action of *ter*.-butyl chloride on phenol in presence of alkali is *p-ter*.-butylphenol. No satisfactory evidence of the production of an isomeric butylphenol has been obtained. If any ether is produced, it is formed in very small quantity and is converted into



the isomeric phenol on sulphonating. The ease with which *p-ter.*-butylphenol is volatilised by steam from a strongly alkaline liquid and the comparative difficulty with which it dissolves in caustic alkali point to its being an extremely weak acid.

The difficulty of obtaining mixed ethers of phenols containing a tertiary alkyl group has been brought under notice since the above experiments were carried out by Spiegel and Sabbath (*Ber.*, 1901, 34, 1946). They found that on heating potassium *p*-nitrophenate with *ter.*-butyl chloride and alcohol under pressure at 140° no trace of ether was obtained; even after adding an alcoholic solution of the chloride to the silver salt of *p*-nitrophenol and allowing the two substances to interact at ordinary temperatures, the *p*-nitrophenol was recovered unchanged. Similar results were obtained when *ter.*-amyl chloride was used.

Observations recorded by Mackenzie (*Trans.*, 1901, 79, 1209, 1216) seem to bear on the same point. He was unable to prepare an ether by the action of benzophenone chloride on sodium phenate (or phenol), the isomeric-4:4'-dihydroxytetraphenylmethane being formed instead; in a similar manner benzal chloride and phenol give dihydroxytriphenylmethane and not the corresponding ether.

The ease with which the tertiary butyl group attaches itself to a carbon atom of the benzene nucleus is brought out very clearly by the production of *ter.*-butylphenol in fair quantity, under such mild conditions, and under circumstances under which the formation of an ether might have been expected. The well-known fact that attempts to prepare homologues of benzene containing the isobutyl group attached to a nuclear carbon atom invariably involve the formation of their *tertiary* isomers (*cf.* Baur, *Ber.*, 1891, 24, 2832—2835; Schramm, *Monatsh.*, 1888, 9, 613—625) is apparently of the same order.

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#### XXXIV.—*The Constitution of the Products of Nitration of Aceto-m-toluidide.*

By JULIUS B. COHEN and HENRY D. DAKIN.

IN the course of some experiments which had for their object the preparation of the trichlorotoluenes from the chlorine derivatives of nitroaceto-*m*-toluidide, it was found that a degree of uncertainty

existed as to the constitution of the nitroacetotoluidide obtained by Beilstein and Kühlberg (*Annalen*, 1871, 158, 348). On reinvestigating the subject, definite evidence was obtained as to the constitution of the substance, and it was also found that a previously overlooked isomeric nitro-compound was formed during the nitration.

Beilstein and Kühlberg describe the nitroaceto-*m*-toluidide as a substance crystallising in red prisms melting at 101—102°. On hydrolysis they obtained a base melting at 133—134°, and showed that on removing the amino-group from this substance, they obtained a liquid nitrotoluene which on subsequent reduction and acetylation gave aceto-*o*-toluidide.

These experiments whilst proving that the nitro-group is in the ortho-position relative to the methyl group, are obviously insufficient to decide between the two possible ortho- and para-positions respectively to the amino-group.

Limpricht (*Ber.*, 1885, 18, 403) ascribes the 2-nitroacetylaminotoluene formula to Beilstein and Kühlberg's compound and reserves the 6-nitro-3-acetylaminotoluene formula for a substance obtained by the partial reduction of a dinitro-compound of unknown constitution, obtained as a by-product in the nitration of toluene. It is not clear that Limpricht had any experimental evidence in support of the constitutions he assigned to the two substances.

Fileti and Crosa (*Gazzetta*, 1888, 18, 298) obtained a base apparently identical with the nitrotoluidine of Beilstein and Kühlberg by heating bromonitrotoluic acid with alcoholic ammonia at 180°. The bromonitrotoluic acid was obtained by the oxidation of bromonitrocymene ( $\text{Me} : \text{NO}_2 : \text{Br} : \text{Pr}^\beta = 1 : 6 : 3 : 4$ ), from which it follows that the nitrotoluidine should be represented as containing its substituent radicles in the following positions:  $\text{Me} : \text{NH}_2 : \text{NO}_2 = 1 : 3 : 6$ . They also showed that on further reducing the base, they obtained a substance melting at 64°, which accords with 2:5-tolylenediamine. 2:3-Tolylenediamine, however, melts at almost the same temperature.

The results of the experiments that follow show that the nitration of aceto-*m*-toluidide results in the formation of two nitro-derivatives. The main product consists of 6-nitro-3-acetylaminotoluene and is identical with the product described by Beilstein and Kühlberg. The nitro-group was proved to occupy position 6, by converting the substance successively into 3-chloro-6-nitrotoluene and 3-chloro-4:6-dinitrotoluene and also by showing that the tolylenediamine obtained by hydrolysis and reduction gave the green colouring matter described by Nietzki (*Ber.*, 1877, 10, 1158) on treatment with *o*-toluidine and ferric chloride. Limpricht's formula is therefore shown to be incorrect.

A smaller quantity of an isomeric nitro-compound was separated by fractional crystallisation from alcohol, and was proved to be 4-nitro-

3-acetylaminotoluene. On hydrolysis, it gave a base which was identical with the product obtained by Staedel and Kolb (*Annalen*, 1890, 259, 224) by heating 4-nitro-*m*-tolyl ethyl ether with ammonia.

The simultaneous formation of *o*- and *p*-derivatives in this case is interesting since the nitration of aceto-*o*-toluidide is thereby shown to be essentially similar to that of its *m*-isomeride. Aceto-*o*-toluidide was originally supposed to give simply the *p*-derivative (Beilstein and Kühlberg, *Annalen*, 1871, 158, 345) but Lellman and Würthner (*Annalen*, 1885, 228, 240) showed that the *o*-compound was also present in quite large quantities.

#### EXPERIMENTAL.

Twenty grams of aceto-*m*-toluidide were added in small portions at a time to 75 grams of freshly distilled fuming nitric acid and 25 grams of glacial acetic acid. The mixture was maintained at about 15°, and about two hours after the whole of the acetotoluidide had been added, the clear reddish solution was poured into water, the precipitated nitroacetotoluidides being crystallised from alcohol. The crystals first deposited were fine, massive, red prisms, which collected in a compact layer at the bottom of the vessel. On further standing, long, yellowish needles were deposited. The two kinds of crystals were separated mechanically as far as possible, and then repeatedly crystallised from alcohol. The prisms, which form the main product of the reaction, melted at 103—104° (Beilstein and Kühlberg give 101—102°). The yellow needles, which amounted to about 15 per cent. of the whole product, melted at 86—87°, and gave on hydrolysis 4-nitro-3-aminotoluene melting at 110—110.5°.

6-Nitro-3-acetotoluidide is readily hydrolysed with boiling hydrochloric acid, the nitrotoluidine hydrochloride crystallising out from the acid solution. On boiling the hydrochloride with water the free base is obtained, and crystallises from hot water or dilute alcohol in long, yellow needles melting at 133—134°.

The conversion of the nitrotoluidine into 3-chloro-4 : 6-dinitrotoluene was carried out as follows : pure nitrotoluidine was converted into the hydrochloride by boiling with a large excess of concentrated hydrochloric acid ; the solution was then cooled in a freezing mixture, and diazotised with solid sodium nitrite. Diazotisation was somewhat slow and required an excess of nitrite, but was eventually complete. On pouring the solution into cold cuprous chloride solution, a rapid evolution of nitrogen occurred, and an almost theoretical yield of liquid chloronitrotoluene was obtained on subsequent distillation in steam. The chloronitrotoluene was next nitrated with fuming nitric acid and con-



centrated sulphuric acid. After the reaction had been completed by warming on the water-bath, the dinitro-compound was precipitated with water and crystallised from alcohol. The substance crystallised in fine, shining leaflets melting at  $90-91^{\circ}$ , and was identical with 3-chloro-4:6-dinitrotoluene (Reverdin and Crépieux, *Ber.*, 1900, 33, 2505). The constitution of the original substance must obviously be 6-nitro-3-aminotoluene, if it can be converted into *o*-toluidine on the one hand, and into 3-chloro-4:6-dinitrotoluene on the other.

6-Nitro-3-acetylaminotoluene readily yields chlorine derivatives when dissolved in acetic and hydrochloric acids and treated with sodium chlorate. So far only preliminary experiments have been made in this direction, but the di- and tri-chloro-derivatives have been obtained as follows.

Nine grams of the nitro-compound were dissolved in 75 c.c. of glacial acetic acid and 37 c.c. of concentrated hydrochloric acid. The solution was then carefully cooled and 4 grams of sodium chlorate dissolved in the minimum amount of water, gradually added in small portions. After some time, water was added and the precipitate crystallised from alcohol. The product was not uniform in appearance and melted indefinitely between  $110-115^{\circ}$ . On analysis, it was found to contain 21.5 per cent. of chlorine corresponding with a mixture of about equal quantities of the mono- and di-chloro-derivatives. The substance was then redissolved in the same acid mixture as before, and a further addition of 2 grams of sodium chlorate made. The substance was subsequently precipitated and repeatedly crystallised from alcohol. Dichloro-6-nitro-3-acetylaminotoluene was obtained in colourless crystals melting at  $181-183^{\circ}$ .

0.0772 gave 0.0854 AgCl.  $\text{Cl} = 27.2$ .

$\text{C}_9\text{H}_8\text{O}_3\text{N}_2\text{Cl}_2$  requires  $\text{Cl} = 27.0$  per cent.

A small quantity of substance was separated which was more insoluble in alcohol than the dichloro-derivative and was apparently 2:4:5-trichloro-6-nitro-3-acetylaminotoluene. It did not melt below  $200^{\circ}$ .

The hydrolysis of the isomeric nitro-acetotoluidide was effected with boiling hydrochloric acid, and the base was precipitated from the acid solution by the addition of caustic soda. It crystallised from alcohol in fine, prismatic needles melting at  $110-110.5^{\circ}$  in agreement with 4-nitro-3-aminotoluene.

### XXXV.—*The Solubilities and Transition-Points of Lithium Nitrate and its Hydrates.*

By FREDERICK GEORGE DONNAN and BRYCE CHUDLEIGH BURT.

THE object of the experiments described in this paper was to examine the various solid phases which can separate from the two-component system, water—lithium nitrate, and to determine the conditions of their existence in contact with the saturated solution.

As the first member of its group, lithium shows many analogies with the elements of the succeeding series, in particular with calcium. In agreement with this, lithium nitrate is a very deliquescent and extremely soluble salt. It is also characterised by a tendency to form supersaturated solutions, resembling calcium chloride in this respect.

The first experiments on the hydrates of lithium nitrate appear to have been those of Kremers (*Jahresberichte*, 1854, 324; *Pogg. Ann.*, 92, 520), who mentions that he obtained a hydrate crystallising in needles and also another form crystallising in rhombohedra which he assumed to be the anhydrous salt. The former he regarded as the hydrate  $\text{LiNO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . The same formula was assigned to it by Troost (*Jahresberichte*, 1857, 140). Both observers obtained this salt by crystallisation below  $20^\circ$ .

According to Dott, however (*Pharm. J.*, 1893, 124, [iii], 215), the hydrate obtained by Kremers and Troost possesses the formula  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ .

Solubility measurements were carried out by Kremers at a few temperatures, but these do not agree well with the results recorded below. Similar discrepancies have been observed in many other cases of this sort, and are chiefly due to the fact that not enough attention was paid by the earlier observers to the securing of constant temperature and complete saturation.

#### *Crystallisation Experiments.*

The salt used in the following experiments was obtained from Kahlbaum and purified by recrystallisation. When a strong solution was cooled down to the ordinary temperature and allowed to crystallise, delicate deliquescent needles were obtained. These were filtered by suction and rapidly dried between folds of filter paper. They proved on analysis to consist of the trihydrate, as shown by the following results:

Found  $\text{H}_2\text{O} = 44.1$ ;  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  requires 43.9 per cent.

On allowing a more concentrated solution to crystallise at a temperature above  $30^{\circ}$ , crystals were obtained having an entirely different appearance. It was found difficult to obtain specimens giving constant results on analysis by simply filtering off and drying in the usual way, probably owing to the rapid solidification of the adherent mother liquor to a mixture of the two hydrates (see p. 339). However, on crystallising in an air-bath at a constant temperature of  $40^{\circ}$  and allowing the selected crystals to dry on filter paper while remaining in the bath, a hydrate was obtained in a state of purity, as shown by the following analyses:

Found  $\text{H}_2\text{O} = 11.6, 11.8$ ;  $\text{LiNO}_3, \frac{1}{2}\text{H}_2\text{O}$  requires 11.5 per cent.

Isothermal crystallisation, at a temperature of  $90^{\circ}$ , yielded a salt which on examination under the microscope appeared to differ in crystalline form from the preceding hydrates. This was evidently the anhydrous nitrate, although the specimens analysed appeared to contain quantities of water varying from 1 to 2 per cent. As the salt is, however, exceedingly deliquescent, this small and variable amount of water may safely be ascribed to the difficulty in obtaining a really dry sample.

#### *Solubilities of the Trihydrate.*

These determinations were carried out by stirring the salt with water, using an apparatus of the form employed by van't Hoff. The arrangements, which were of the usual description, included a water-thermostat, an Ostwald toluene thermo-regulator, with a small Heinrici hot-air motor to drive not only the thermostat-stirrer but also the stirrers of two solubility vessels. The thermometer employed was divided into tenths, and standardised by comparison with Travers' hydrogen thermometer.

Usually, the solutions were rapidly stirred for 24—30 hours to attain saturation-equilibrium. The stirrer was then stopped, and after the particles of salt had been given a short time to settle, a portion of the solution was withdrawn by means of a previously warmed pipette, to the lower end of which a small filtering tube containing glass wool was attached by indiarubber tubing. The solution thus removed was at once poured into one or more small weighed Erlenmeyer flasks of Jena glass. These were placed in an air-bath maintained at  $180^{\circ}$ , and connected to a water-pump through a drying bottle containing strong sulphuric acid. The evaporation, which was thus carried out in a vacuum desiccator at  $180^{\circ}$ , was continued until the anhydrous salt was of constant weight.

The analyses recorded in this paper were all carried out in this way.



Each solubility result contained in the following, as well as in the other tables, is the mean of two concordant determinations (carried out simultaneously in different solubility vessels.

1. *Solubilities of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ .*

| Temperature .....  | 0·10° | 10·50° | 12·10° | 13·75° | 19·05° | 22·10° |
|--|-------|--------|--------|--------|--------|--------|
| Concentration (parts by weight of dry anhydrous salt in 100 parts by weight of solution) ..... | 34·8  | 37·9   | 38·2   | 39·3   | 40·4   | 42·9   |

The lowest temperature was obtained in a bath of ice and water.

On attempting to make solubility measurements with this hydrate at higher temperatures, the solubility was found to increase very rapidly, evidently indicating its rapid approach to a point of infinite solubility, that is, to the true melting point of the trihydrate.

An approximate preliminary estimate of this temperature was obtained by melting the salt in a tube and observing the melting point with an ordinary thermometer; the trihydrate was found to melt at about 30° to a perfectly clear liquid.

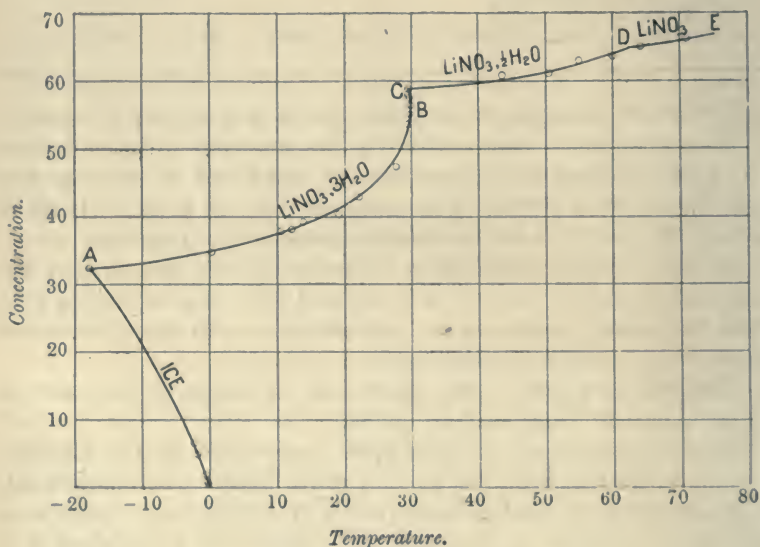
The exact position of this point and the course of the curve on either side were determined as follows.

Solutions corresponding to the upper portion, *BC*, of the solubility curve of the trihydrate contain less water than the crystallised salt. They are therefore obtained most readily by melting the trihydrate and driving off a portion of the water. The amount of water expelled in this operation must be controlled by frequent weighing in order to avoid reaching the point *C*, which would cause the separation of the next phase. Solutions corresponding to points on the right of *BC* and below *C* will deposit the trihydrate on cooling. A weighed amount of such a solution of known concentration being placed in a Beckmann freezing-point tube fitted with thermometer and stirrer, the tube was allowed to cool until the solution was slightly supercooled, after which the tube was inserted in the air jacket, the latter being packed round with sheep's wool contained in a large beaker. Crystallisation having been started by the introduction of a minute crystal of the trihydrate, the mixture was kept constantly stirred and the maximum temperature noted, observations being made for 20—30 minutes, during which time the temperature remained practically constant.\* After a preliminary observation, more accurate experiments were made by employing a

\* The technique of measurements of this kind has been recently developed by F. A. Lidbury (*Zeits. physikal. Chem.*, 1902, 39, 453).

constant supercooling of  $0.5^\circ$ . The first point thus determined was quite close to *C*. Lower points on the curve were obtained by successive dilutions made *in situ*. For this purpose, very thin sealed glass bulbs containing small weighed quantities of water were introduced into the tube and broken by means of the stirrer. The temperatures thus determined on the arbitrary scale of the Beckmann thermometer were referred to the standard thermometer by comparison of the two scales immediately before and after the observations.

The melting point of the trihydrate (see point *B* in the figure)



Solubility-curves of the system,  $\text{LiNO}_3\text{—H}_2\text{O}$ .

corresponds with a point on the curve where the tangent is vertical, and could now be determined graphically, since points on either side in its immediate neighbourhood were known; it was found to be  $29.88^\circ$ , a value agreeing sufficiently well with the direct determination of this temperature. The following table contains the results of the experiments made in the manner described above. These data enable the form of the solubility curve of the trihydrate in the neighbourhood of its melting point to be determined with considerable precision.

2. *Temperature-Concentration Data for  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  in the Neighbourhood of its Melting Point.*

|  |        |        |        |        |        |        |        |
|--|--------|--------|--------|--------|--------|--------|--------|
| Temperature .....  | 27·55° | 29·47° | 29·78° | 29·87° | 29·86° | 29·64° | 29·55° |
| Concentration (parts $\text{LiNO}_3$<br>per 100 parts of solution).. | 47·30  | 53·67  | 55·09  | 56·42  | 56·68  | 57·48  | 58·03  |

*Solubilities at Temperatures above 30°.*

In the case of solubility measurements carried out at higher temperatures it was unsafe to employ a pipette in withdrawing the saturated solution, so the latter was blown over into a small weighed Erlenmeyer flask of Jena glass. To the end of the connecting tube which passed through the rubber stopper of the solubility vessel a small filtering tube containing glass-wool was attached by indiarubber tubing, the whole apparatus being completely immersed in the thermostat.

The solid phase employed in these determinations was the semihydrate obtained as described previously by isothermal crystallisation at 40°. As before, stirring was continued for a long time, in order to ensure complete saturation and also to allow time for any changes occurring in the solid phase. As will be seen, such changes did actually occur at the higher temperatures. The solubilities thus determined are given in the following table:

3. *Solubilities at Higher Temperatures.*

|                     |       |       |       |       |       |       |
|---------------------|-------|-------|-------|-------|-------|-------|
| Temperature .....   | 43·6° | 50·5° | 55·0° | 60·0° | 64·2° | 70·9° |
| Concentration ..... | 60·8  | 61·3  | 63·0  | 63·6  | 64·9  | 66·1  |

Concentration is expressed in the same units as before, and the numbers in the lower line are the means of independent determinations. On plotting these data it was apparent that a break existed at about 61° (see point *D* in the figure. Owing to a slight error in "adjustment" of the curve *CD* shown in the diagram, the point *D* is represented as corresponding to a rather higher temperature).

In order to confirm the existence of this transition-point and to obtain an independent determination of its position, measurements



were made with a van't Hoff dilatometer, the arrangements for filling being such that both dilatometer and paraffin were well exhausted before the latter was introduced into the capillary. As we had reason to suppose that the break in the solubility curve corresponded with a transition to the anhydrous salt, a little of the latter was added to the slightly moist semihydrate contained in the dilatometer bulb. The following is a brief record of the observations made:

Slow heating up to  $62.5^{\circ}$  in thermostat. Regular expansion at  $62.5^{\circ}$  sudden increase of expansion.

Rapid cooling to  $60.7^{\circ}$ . Ascending value not recovered; remained overnight at this temperature; meniscus returned to original (ascending) point.

Slow heating up to  $62^{\circ}$ ; expansion (isothermal) occurs.

Contents of dilatometer brought to the state of half transition as recommended by van't Hoff; neither expansion nor contraction at  $61^{\circ}$  during 48 hours. At  $61.4^{\circ}$  an expansion of about 5 mm. in the course of several hours.

The transition-point therefore lies between  $60.7^{\circ}$  and  $61.4^{\circ}$ , the mean of which,  $61.05^{\circ}$ , agrees very well with the value obtained from the solubility curves. We may therefore take  $61.1^{\circ}$  as being a fairly close approximation to the transition-temperature.

No evidence of any further transition was observed, even when the dilatometer was heated up to  $90^{\circ}$ . As the isothermal crystallisation at temperatures of  $75$ — $90^{\circ}$  invariably yielded the anhydrous salt, there is no doubt that the above transition-point corresponds with the change, semihydrate  $\rightarrow$  anhydrous salt + saturated solution.

#### *Determination of Point C.*

The composition of the solution corresponding to the maximum temperature point *B* of the curve *ABC* is the same as that of the trihydrate. A corresponding maximum-temperature point for the semihydrate would lie on the metastable portion of *CD* beyond *D*. The composition of the solution represented by the point *C* lies therefore between the compositions of the two hydrates. Hence if heat be removed from a solution the composition of which corresponds with *C* it will solidify gradually (provided supersaturation is guarded against) to a mixture of the trihydrate and semihydrate. In this way an independent determination of the position of *C* was carried out (its position being already known approximately from the solubility-curves).

A saturated solution of  $\text{LiNO}_3, \frac{1}{2}\text{H}_2\text{O}$ , contained in a tube insulated by a vacuum-vessel packed round with sheep's wool, was allowed to cool

slowly to a temperature below the approximate position of *C*, crystallisation being then started by dropping in small crystals of both hydrates. The thick paste thus obtained was stirred vigorously and the steady maximum temperature noted. In this way the temperature corresponding with *C* was found to be  $29.6^{\circ}$ .

### *Cryohydrate-Point and Ice-Curve.*

The lower portion of the ice-curve OA (from zero to  $-2.5^{\circ}$ ) was determined in the ordinary way in the Beckmann apparatus. Owing to the highly deliquescent nature of the lithium nitrate, weighed quantities of a solution of known concentration contained in thin sealed glass bulbs were added to a known weight of water, and the bulbs broken by the stirrer.

The position of the cryohydrate-point A was fixed by ascertaining the steady temperature assumed by a mixture of finely powdered ice and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , contained in a tube well protected from external heating by a packing of ice. The corresponding solution was also analysed. The thermometer employed was standardised at  $0^{\circ}$ , and its scale calibrated from  $0^{\circ}$  to  $-20^{\circ}$ . The cryohydrate-temperature determined in this manner was found to be  $-17.8^{\circ}$ .

The following is a summary of the quadruple-points, melting-points, and equilibrium-curves of the lithium nitrate—water system. The letters refer to the diagram accompanying this paper.

#### *I. Quadruple-points :*

A. Cryohydrate-point of the trihydrate ( $-17.8^{\circ}$ ).

C. Transition-point, trihydrate + semihydrate  $\rightleftharpoons$  saturated solution ( $29.6^{\circ}$ ).

D. Transition-point, semihydrate  $\rightleftharpoons$  anhydrous salt + saturated solution ( $61.1^{\circ}$ ).

#### *II. Melting-points :*

O and B. Melting-points of ice and trihydrate ( $29.88^{\circ}$ ) respectively.

#### *III. Equilibrium-curves :*

OA, ABC, CD, and DE, correspond with the solid phases, ice,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and  $\text{LiNO}_3$  respectively.

A determination of the solubility of the trihydrate at  $10^{\circ}$  (made at an early stage of our work) which did not agree with any subsequent determinations suggested the possible existence of another phase. Thermometric experiments gave no indication, however, of any break in the cooling-curve of the system,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  + saturated solution. Furthermore, the cryohydrate-point and the point corresponding with  $0^{\circ}$  lie on a curve continuous with the solubility-determinations at higher temperatures. The solubility-determination in question must

therefore have been vitiated by some large error, and accordingly it has not been shown on the diagram.

In conclusion, we desire to express our thanks to Professor Ramsay for the interest which he has taken in our work.

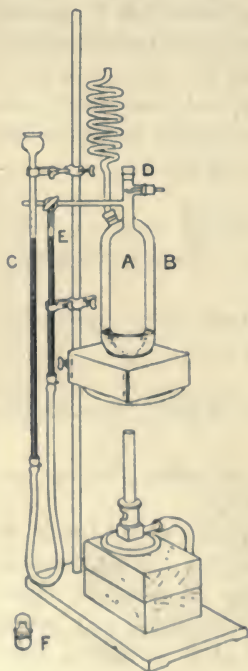
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### XXXVI.—*A New Vapour Density Apparatus.*

By JOHN S. LUMSDEN, D.Sc., Ph.D.

THERE are two deductions from the gas laws and Avogadro's hypothesis which furnish the principles upon which are based the methods for determining the molecular weights of substances which can exist in

FIG. 1.



the gaseous state. These are: (1) the molecular weights of all substances when in the state of gas, under similar conditions of temperature and pressure, occupy the same volume; and (2) the molecular weights of all substances in the state of gas, when occupying the same volume and at the same temperature, exert the same pressure.

Methods based on the first principle require the determination of that weight of a substance which, under like conditions of temperature and pressure, will occupy the same volume as a definite weight of a standard substance; whilst an application of the second principle requires a determination of that weight which, occupying a similar volume and at the same temperature, will exert the same pressure as a definite weight of the standard substance.

Two grams of hydrogen gas are taken as the standard and, adopting 0.0899 gram as the weight of 1 litre of hydrogen at 0° and 760 mm. pressure, 2 grams occupy 22.24 litres.

The apparatus here described is based on the second principle, being an instrument of constant volume in which the temperature remains unaltered during the experiment and the pressure produced by the vapour of the substance is determined.

It consists of a bulb, *A* (Fig. 1), surrounded by a heating jacket, *B*,



and attached to a manometer, *C*. A weighed quantity of substance is dropped into the bulb, there converted into vapour, and the pressure measured before diffusion takes place.

The bulb has a capacity of 100 c.c., and the inlet-tube, *D*, having a width of 8 mm., has a side-tube for the insertion of a glass rod to support the substance before it is dropped into the bulb. A tube of narrow bore, furnished with a three-way tap, leads to the manometer. Just below this tap is fused on a piece of wider tube of the same calibre as the measuring tube of the manometer, the measuring tube in this case being simply a thistle funnel graduated in millimetres. A mark *E* is made on the fixed limb of the manometer so that, the mercury being raised to that height, it will always enclose the same volume of gas.

The heating jacket is provided with a spiral air condenser which has proved to be quite efficient, as no liquid of lower boiling point than water is used.

Heat is obtained from a small bunsen flame, and an asbestos box, with a hole in the top and a wire gauze bottom, has been found to be an excellent support for the apparatus.

It is essential that the inlet tube where the substance is placed should be kept cool, and an asbestos card, resting on the top of the outer jacket, is used to reflect the heat downwards.

In order to perform an experiment, the liquid in the outer jacket is boiled for at least fifteen minutes to ensure that the whole apparatus has been heated and the temperature is constant. The temperature in the inside of the bulb should then be that of the boiling point of the heating liquid, and this should be ascertained by placing a thermometer in the bulb for a few minutes.

The tap being open to the air, the mercury is levelled to the mark, and the substance in a tiny glass capsule dropped on the support. The rubber stopper is then inserted, the tap closed to the air, and the capsule, being released by turning the support, falls into the bulb. While the substance is being vaporised, the graduated measuring tube is raised to keep the level of mercury near the mark. Within a minute, the pressure becomes constant, the manometer tubes are placed close together, the mercury adjusted accurately to the mark, and the difference in level in the two tubes carefully measured. This reading is the pressure due to the vapour of the substance. The manometer tube may now be returned to the clamp, the tap opened to the air, and the stoppers removed. A glass tube is then inserted into the bulb and the substance is cleaned out either by blowing in air, or better, by attaching the tube to a pump and sucking out the vapour.

After removing the tube, the apparatus attains its former temperature in ten minutes and is ready for another determination.

When used as an instrument to give absolute measurements, the capacity of the apparatus must be known. This is easily found by filling the bulb and tubes with water from a burette, or by finding the weight of the apparatus empty and then filled with water.

The capacity of the bulb, the temperature, and the pressure due to the vapour, being known, the molecular weight is deduced thus:

If  $V$  is the capacity of the apparatus,  $P$  the barometric pressure, and  $p$  the increase in pressure due to the vapour of the substance, the volume causing pressure  $p$  is  $Vp/P$ . For, volume  $V$  would become with the new vapour  $V(P+p)/P$  and the volume of vapour would be  $V(P+p)/P - V = Vp/P$ .

This volume at  $P$  and  $t^\circ$  becomes at 760 mm. and  $0^\circ$ ,  $Vp273/760(t+273)$ . The weight  $w$  of substance to obtain this volume of vapour is known, and as we assume the molecular weight to be the weight of substance which occupies a volume of 22.24 litres at  $0^\circ$  and 760 mm. pressure, it is

$$\frac{22.24(t+273)760}{V273} \cdot \frac{w}{p},$$

or the molecular weight =  $Kw/p$ .

As  $V$  is constant for the same apparatus,  $K$  varies directly as the absolute temperature.

The simplicity of this method for determining molecular weights is apparent. No barometric reading is necessary, only the change in pressure requires to be measured. When the constant is found and the substance weighed, the actual experiment does not occupy more than two minutes and the molecular weight may be calculated in another two minutes.

The following are some of the values found for a series of successive experiments:

|  | <i>w.</i> | <i>p.</i> | <i>Kw/p.</i> | Mol. wt.<br>calculated. |
|--|-----------|-----------|--------------|-------------------------|
| <i>Heating liquid—Water. V = 111.5 c.c. t = 100°. log. K = 3163.</i> |           |           |              |                         |
| Acetone .....  | 0.0448    | 16.1      | 57.65        | 57.61                   |
|  | 0.0386    | 13.9      | 57.53        | —                       |
| Chloroform... ..   | 0.0870    | 15.2      | 118.60       | 118.45                  |
|  | 0.0479    | 8.4       | 118.10       | —                       |
| Benzene .....  | 0.0526    | 14.0      | 77.84        | 77.46                   |
|  | 0.0377    | 10.1      | 77.32        | —                       |
| Ether .....  | 0.0461    | 12.9      | 74.03        | 73.52                   |
|  | 0.0510    | 14.4      | 73.36        | —                       |

|  | w. | p. | Kw/p. | Mol. wt.<br>calculated. |
|--|----|----|-------|-------------------------|
|--|----|----|-------|-------------------------|

*Heating liquid—Xylene.*  $V=113$ .  $t=138^{\circ}$ .  $\log K=3525$ .

|               |        |      |       |       |
|---------------|--------|------|-------|-------|
| Toluene ..... | 0.0514 | 12.6 | 91.85 | 91.37 |
|               | 0.0530 | 13.0 | 91.81 | —     |
| Water .....   | 0.0235 | 28.7 | 18.44 | 17.88 |
|               | 0.0164 | 20.3 | 18.19 | —     |

*Heating liquid—Aniline.*  $V=113$ .  $t=183^{\circ}$ .  $\log K=3977$ .

|                          |        |      |       |        |
|--------------------------|--------|------|-------|--------|
| Ethylene dibromide ..... | 0.0796 | 10.7 | 186.1 | 186.54 |
|                          | 0.1131 | 15.1 | 187.2 | —      |
| Anisole .....            | 0.0545 | 12.6 | 108.1 | 107.25 |
|                          | 0.0599 | 13.9 | 107.4 | —      |

*Heating liquid—Nitrobenzene.*  $V=113$ .  $t=206^{\circ}$ .  $\log K=4190$ .

|               |        |      |       |       |
|---------------|--------|------|-------|-------|
| Phenol .....  | 0.0530 | 14.9 | 93.35 | 93.34 |
|               | 0.0656 | 18.5 | 93.05 | —     |
| Aniline ..... | 0.0536 | 15.2 | 92.55 | 92.39 |
|               | 0.0552 | 15.7 | 92.26 | —     |

*Heating liquid—Quinoline.*  $V=113$ .  $t=230^{\circ}$ .  $\log K=4403$ .

|                   |        |      |       |        |
|-------------------|--------|------|-------|--------|
| Camphor.....      | 0.0550 | 10.0 | 151.6 | 150.98 |
|                   | 0.0682 | 12.4 | 151.6 | —      |
| Naphthalene ..... | 0.0375 | 8.1  | 127.6 | 127.10 |
|                   | 0.0364 | 7.9  | 127.0 | —      |

The accuracy of the results depends very much on the rapidity with which the substance is vaporised, and this is the more important the smaller the molecular weight, since a vapour which diffuses rapidly may reach the colder part of the apparatus before a measurement of pressure can be made.

In order to increase the rate of vaporisation, the temperature of the heating liquid should be not less than  $30^{\circ}$  to  $40^{\circ}$  above the boiling point of the substance. It is also advantageous to weigh the substance in an open thin glass capsule provided only with a cap (Fig. 1, F). The capsule is placed in a hole in a cork while being weighed, and until it is dropped into the neck of the apparatus the cap is kept on. Only very volatile substances need be weighed in a stoppered tube.



When the capsule drops into the bulb, it may fall in such a way that it is rapidly emptied, but it may also lie on the bottom of the bulb touching the glass at only a few points, and the liquid is slowly heated by the surrounding air. By having a small quantity of fusible metal in the bulb this is prevented: the capsule falls on the liquid metal so that there is good contact and the contents are instantly expelled.

At temperatures above  $200^{\circ}$  the apparatus may, with advantage, be used as a comparative instrument.

A quantity of a substance, the molecular weight of which is known, is dropped into the bulb, and from the pressure obtained, the pressure which the molecular weight in milligrams would produce is found. This may be called the molecular pressure.

A portion of a substance, the molecular weight of which is required, is then dropped into the bulb, and from the pressure produced, the weight in milligrams which would cause the molecular pressure is calculated. This corresponds to the molecular weight.

The best substance to use for comparison is sodium hydrogen carbonate. When this is heated, two molecules give one molecule of carbon dioxide and one molecule of water, or one molecular weight of sodium hydrogen carbonate gives one molecular volume of gas. The decomposition is rapid and complete, and as there is no possibility of change in composition of the products at a high temperature this is a better comparison substance than any organic compound.

The following example of the determination of the molecular weight of mercury will explain the method: 19.6 milligrams of sodium hydrogen carbonate dropped into the bulb produced a pressure of 9.8 cm., the molecular weight, 83.43 mg., will produce a pressure of 41.72 cm.

51.4 milligrams of mercury dropped into the bulb at the same temperature caused a pressure of 10.8 cm. The weight of mercury which would produce a pressure of 41.72 cm. is therefore  $\frac{41.72 \times 51.4}{10.8} =$

198.6 mg. The true molecular weight of mercury is 198.8.

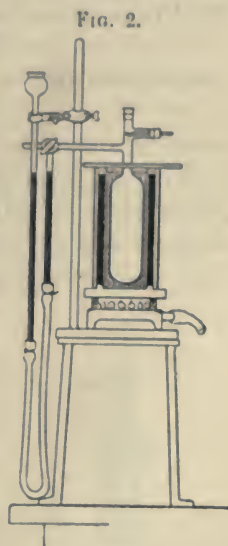
In using this comparison method, neither the capacity of the apparatus nor the temperature requires to be known, the only essential being that the temperature must remain constant for ten minutes to allow of both substances being vaporised under similar conditions.

The work may be still further simplified where a liquid of constant boiling point can be used as the heating agent. Since the pressure produced by the molecular weight in milligrams is constant for the same temperature, it need only be determined once, and then the comparison substance is no longer required. The molecular pressures may also be found for a series of temperatures, and a temperature-pressure

curve, which is a straight line, prepared for the instrument. With the assistance of such a curve, when the temperature in the apparatus has been found by a thermometer and the corresponding molecular pressure noted, the molecular weight is got by simply measuring the pressure produced by a weighed portion of the substance.

The apparatus shown in Fig. 2 was employed for vaporising substances at high temperatures. It consists of two concentric tubes screwed to an iron sole. The outer tube is of stout iron, and the inner one of thin brass. Between the tubes, tin, lead, zinc, or antimony may be placed to act as the heating liquid. The bulb, embedded in aluminium powder or zinc dust, occupies the inner tube. Heat is obtained from a ring burner, and the upper part of the apparatus is protected by interposing sheets of asbestos.

When the metal is melted, by regulating the burner the temperature can be kept constant for an hour. Using this apparatus with melted lead as the heating agent, the following results were obtained :

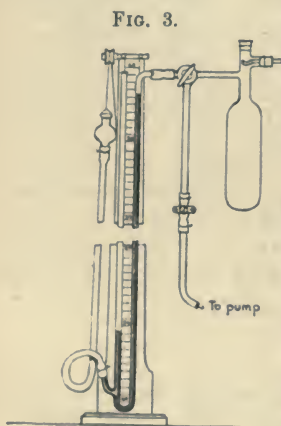


|                           | <i>w.</i> | <i>p.</i> |                               |                      |
|---------------------------|-----------|-----------|-------------------------------|----------------------|
| NaHCO <sub>3</sub> .....  | 0·0509    | 24·2      | Mol. press. $K=39\cdot68$ cm. |                      |
|                           |           |           | $Kw/p.$                       | Mol. wt. calculated. |
| Anthracene .....          | 0·0410    | 9·2       | 176·8                         | 176·74               |
| Diphenyl .....            | 0·0378    | 9·8       | 153·1                         | 152·92               |
|                           |           |           |                               |                      |
| NaHCO <sub>3</sub> .....  | 0·0474    | 22·1      | $K=38\cdot90$ cm.             |                      |
|                           |           |           | $Kw/p.$                       | Mol. wt. calculated. |
| Naphthalene .....         | 0·0540    | 16·6      | 126·6                         | 127·1                |
|                           |           |           |                               |                      |
| NaHCO <sub>3</sub> .....  | 0·0508    | 24·2      | $K=39\cdot75$ cm.             |                      |
|                           |           |           | $Kw/p.$                       | Mol. wt. calculated. |
| Phenanthrene .....        | 0·0448    | 10·1      | 176·3                         | 176·74               |
|                           |           |           |                               |                      |
| NaHCO <sub>3</sub> ... .. | 0·0220    | 10·6      | $K=40\cdot21$ cm.             |                      |
|                           |           |           | $Kw/p.$                       | Mol. wt. calculated. |
| Mercuric chloride .....   | 0·0999    | 14·9      | 269·6                         | 269·16               |
|                           |           |           |                               |                      |
| NaHCO <sub>3</sub> .....  | 0·0196    | 9·8       | $K=41\cdot72$ cm.             |                      |
|                           |           |           | $Kw/p.$                       | Mol. wt. calculated. |
| Mercury .....             | 0·0514    | 10·8      | 198·6                         | 198·8                |

*Estimation of Water of Crystallisation.*

|                            | <i>w.</i> | <i>p.</i> |              |  |
|----------------------------|-----------|-----------|--------------|--|
| NaHCO <sub>3</sub> .....   | 0.0248    | 12.5      |              | <i>K</i> = 42.06 cm.   |
|                            |           |           |              | Weight with  |
|                            |           |           | <i>Kw/p.</i> | 5H <sub>2</sub> O.      CuSO <sub>4</sub> , 5H <sub>2</sub> O. |
| Copper sulphate crystals.. | 0.0212    | 17.9      | 49.79        | 248.95      247.85   |
|                            |           |           |              | Weight with  |
|                            |           |           |              | 2H <sub>2</sub> O.      BaCl <sub>2</sub> , 2H <sub>2</sub> O. |
| Barium chloride crystals.  | 0.0444    | 15.3      | 120.0        | 240.0      242.5   |

As the measurement of the change in pressure due to the vapour of a substance is all that is required in order to determine the molecular weight, it does not matter what the pressure in the bulb of the apparatus may be before an experiment. Hence a substance may be vaporised under diminished pressure. The apparatus arranged for this purpose is shown in Fig. 3, where the horizontal arm of the three-way tap is connected with a fixed manometer and the bulb may be exhausted by the vertical tube.



To perform an experiment, the bulb is heated, the weighed substance placed on the support, and the rubber stopper inserted. The tap is fully opened, and the pressure in the bulb being reduced to the desired amount, the clip on the exhaust tube is screwed tight. The level of the mercury in the open limb of the manometer having been noted, the capsule is dropped in and the mercury reservoir raised to keep

the capacity of the bulb constant. In less than a minute the substance is vaporised and the new level of the mercury is noted. An apparatus for finding molecular weights under diminished pressures, similar in principle to this but much larger and less sensitive, is described by Bleier and Kohn (*Chem. Centr.*, 1899, 2, 737).

The following results were obtained with nitrobenzene as the heating liquid, and sodium hydrogen carbonate to get the molecular pressure.

*Molecular pressure*  $K=24.23$  c.m.

|                                    | <i>w.</i> | <i>p.</i> | $Kw/p.$ | Mol. wt. calculated. |
|------------------------------------|-----------|-----------|---------|----------------------|
| boiling point of nitrobenzene..... | 0.0370    | 8.5       | 105.4   | 105.25               |
| produced by sodium chloride .....  | 0.0469    | 7.1       | 160.1   | 159.73               |
| same temperature .....             | 0.0418    | 8.0       | 126.6   | 127.10               |
| comparison substance .....         | 0.0532    | 8.5       | 151.7   | 150.98               |

also be found for a



Any of the above forms of the apparatus may be used filled with an inert gas instead of air.

The inlet tube for the gas passes to the bottom of the bulb and may be closed with a clip, the tap shut to the air, and the experiment conducted in the usual way.

The adaptability of this apparatus for different temperatures and pressures, its accuracy—at least equal to a Victor Meyer apparatus—its small size and cheapness, the speed with which the experiment is done, and the simplicity of the calculation, make it a most useful instrument for ordinary work in the laboratory.

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DUNDEE.

### XXXVII.—*A New Form of Pyrometer.*

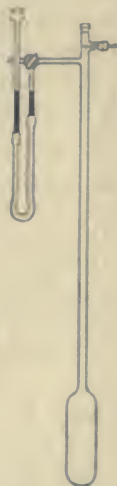
By JOHN S. LUMSDEN, D.Sc., Ph.D.

SINCE the pressure exerted by a given volume of gas varies as the absolute temperature, if the pressures at two temperatures are measured and one temperature is known, the other can be calculated. For short ranges of temperature, an air thermometer of constant volume, connected with a mercury gauge, may be used to measure the pressures produced at the known and unknown temperatures; but such an instrument cannot be employed if there is much difference between the temperatures, owing to the great expansibility of air.

This difficulty may be overcome and any temperature found by using a modification of the apparatus described in the preceding paper. The annexed drawing shows a tube of convenient length and about one centimetre in diameter, ending in a bulb with a capacity of 100—200 c.c.

The top of the tube has a branch for inserting a support for a capsule containing a substance which is to be vaporised, and a narrow tube leads to a manometer.

When the substance is dropped into the bulb, the vapour produced compresses the air above it, but the bulb being many times larger than the volume of the vapour, there is not much displacement of heated air, and the pressure developed can be measured before the vapour diffuses to a place where condensation could take place.



With such an instrument, containing air at the atmospheric pressure, when equal weights of a substance are dropped into the bulb at different temperatures, the pressures produced are proportional to the absolute temperatures. This is the same law as for the air thermometer, but the principle is readily seen to be different.

There is no limit to the range of the instrument so long as the capacity remains unaltered, and it thus forms a simple pyrometer by which temperatures may be ascertained with an accuracy of a few degrees.

To use the apparatus, the pressure produced by a weighed quantity of substance at a known temperature is first determined. This is done by heating the instrument in the vapour of a constant-boiling liquid or by other means, and measuring the pressure produced when a weighed quantity of substance is vaporised in the bulb.

This determination has only to be made once, and it might be done by the maker of the instrument, who would supply the information with respect to temperature and pressure. The bulb is now placed where the unknown temperature has to be found, and the pressure produced from a weighed quantity of substance is measured. The pressures produced at the two temperatures from equal weights of substance are then calculated, and these are proportional to the absolute temperatures. An example will explain the process :

The bulb was heated in the vapour of boiling quinoline at  $230^{\circ}$  and 0.0439 gram of sodium hydrogen carbonate dropped in. The pressure developed was 14.5 centimetres, or one gram would produce a pressure of 330.3 centimetres.

The bulb was then placed in melted lead, and 0.0509 gram of sodium hydrogen carbonate caused a pressure of 24.2 centimetres. The pressure for one gram was, therefore, 475.4 centimetres.

$p/p_1 = T/T_1$ ,  $T_1 = \frac{330.3 \times 503}{475.4} = 724.1$ , or the lead had a temperature of  $451^{\circ}$ .

If the internal volume of the instrument is known, the temperature of the bulb may be found without performing a comparison experiment at a known temperature if a substance of definite molecular weight is used to produce the vapour. Let a weight  $w$  of a substance having a molecular weight  $M$  be vaporised in an instrument of volume  $V$  and produce a pressure  $p$ , the temperature of the vapour is found from the following considerations :

The pressure in the instrument increases from the barometric pressure  $P$  to  $P+p$ , the volume at pressure  $P$  would therefore increase from  $V$  to  $\frac{V(P+p)}{P}$ , and the vapour would have a volume of

$\frac{V(P+p)}{P} - V = \frac{Vp}{P}$ . This volume at  $P$  and  $t^\circ$  becomes at 760 mm. and  $t^\circ$ ,  $\frac{Vp}{760}$ .

The volume of gas produced from a weight  $w$  of a substance having a molecular weight  $M$  is  $\frac{22.24w}{M}$  at 760 mm. and  $0^\circ$ .

We have now the two volumes occupied by a gas at  $0^\circ$  and  $t^\circ$ , under the same pressure, and these volumes being proportional to the absolute temperatures,  $(t^\circ + 273) = \frac{VM}{22.24 \times 760} \cdot \frac{p}{w}$ , or for the same instrument and using the same substance to produce the vapour,  $t^\circ = K \frac{P}{w} - 273$ .

Example: Experiment to find the boiling point of quinoline. 0.0364 gram of naphthalene, molecular weight 127.1, vaporised in a bulb of 113 c.c. capacity, heated by the vapour from boiling quinoline, caused a pressure of 7.9 centimetres of mercury. Using the above formula,  $t^\circ = 503.4 - 273 = 230.4^\circ$ . The quinoline boiled at  $230^\circ$ .

Sodium hydrogen carbonate, contained in a little capsule of lead foil, is a good substance to use for the production of vapour. The lead melts and the powder is instantly decomposed. Any other substance giving a vapour may be used, but the best material would be one from which a permanent gas was evolved.

The bulb of the apparatus may be made of glass, porcelain, or metal, and may have any convenient shape. The error due to expansion of the bulb is small, as an increase of 1 c.c. on a bulb of 100 c.c. would only alter the result about  $2^\circ$ , and this would be proportionately less the larger the bulb.

UNIVERSITY COLLEGE,  
DUNDEE.

### XXXVIII.—The $\alpha\beta$ -Dimethylglutaric Acids, and the Separation of *cis*- and *trans*-Forms of Substituted Glutaric Acids.

By JOCELYN FIELD THORPE and WILLIAM J. YOUNG.

OF the four possible forms of dimethylglutaric acid, the  $\alpha\alpha'$ -derivative,  $\text{CO}_2\text{H} \cdot \text{CH}(\text{Me}) \cdot \text{CH}_2 \cdot \text{CH}(\text{Me}) \cdot \text{CO}_2\text{H}$ , in its *cis*- and *trans*-forms, and the  $\beta\beta$ -acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{Me})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , have already been known for a considerable time, whilst the  $\alpha\alpha$ -acid,  $\text{CO}_2\text{H} \cdot \text{C}(\text{Me})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,



which was first prepared from  $\text{Me}\cdot\text{CO}\cdot\text{C}(\text{Me})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , by treatment with alkaline bromine solution (Tiemann, *Ber.*, 1895, 28, 2176; Perkin, *Trans.*, 1898, 73, 846), has now been synthesised from ethyl  $\alpha\alpha$ -dimethylacetonedicarboxylate by reduction, first with sodium amalgam, and then with hydriodic acid (Perkin and Miss Smith, this vol., p. 8), and its constitution thus not only clearly established, but its properties thoroughly investigated.

The  $\alpha\beta$ -acids,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{Me})\cdot\text{CH}(\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , on the other hand, have only been very imperfectly investigated.

By the action of ethyl sodiomethylmalonate on ethyl  $\gamma$ -chlorobutyrate, Montemartini (*Gazzetta*, 1896, 26, ii, 280; *Ber.*, 1896, 29, 2058) obtained a mixture of two acids, one of which melted at  $63^\circ$ , whilst the other consisted of a syrup, which showed no tendency to crystallise.

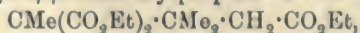
The former he identified as  $\alpha$ -methyladipic acid, and the latter he considered to be  $\alpha\beta$ -dimethylglutaric acid, owing to the fact that he prepared the same syrup by adding hydrocyanic acid to ethyl  $\beta$ -methyllevulinate,  $\text{MeCO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , and reducing the hydrolysed nitrile with hydriodic acid.

His acid boiled at  $200^\circ$  under diminished pressure, undergoing at the same time partial conversion into a liquid anhydride; he also prepared the anilic acid and the anil, both of which were liquids at the ordinary temperature.

Another  $\alpha\beta$ -dimethylglutaric acid is described by Blaise (*Bull. Soc. chim.*, 1896, [iii], 15, 1238), who prepared it by the action of potassium cyanide on dimethyl-2:3-butanolid; it melted at  $82\text{--}83^\circ$ , and yielded an anhydride boiling at  $275\text{--}283^\circ$ , which gave an anilic acid melting at  $147\text{--}148^\circ$ .

The difficulty in synthesising glutaric acids substituted both in the  $\alpha$ - and  $\beta$ -positions is explained by the fact that the ordinary methods for preparing alkyl glutaric acids by the aid of ethyl malonate do not succeed; thus, neither ethyl sodiomethylmalonate nor ethyl cyano-propionate react, under the usual conditions, with ethyl salts of  $\alpha\beta$ -unsaturated acids to form condensation products; further, the products derived from the action of ethyl sodiocyanoacetate or ethyl sodiomalonate on, for example, ethyl  $\beta$ -methylacrylate, and which therefore contain the complex  $-\text{CH}(\text{CO}_2\text{Et})_2$  or  $-\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , do not react with sodium ethoxide to form sodium derivatives (Perkin and Thorpe, *Trans.*, 1899, 75, 50).

In a previous paper (*ibid.*), it was shown that although ethyl  $\beta\beta$ -dimethylpropanetricarboxylate,  $(\text{CO}_2\text{Et})_3\cdot\text{CH}\cdot\text{C}(\text{Me})_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , does not react with sodium ethoxide, and therefore cannot be used in the preparation of ethyl  $\alpha\beta\beta$ -trimethylpropanetricarboxylate,



yet, by taking advantage of the fact that a sodium compound is the

first product formed in the condensation of ethyl sodiomalonate and ethyl dimethylacrylate, a good yield of the methyl derivative could be obtained by treating this sodium compound directly with methyl iodide. It was further shown that the substitution of ethyl cyanoacetate for ethyl malonate in these reactions considerably increased the yield of the condensation product.

In this way, the syntheses of  $\alpha\beta\beta$ -trimethylglutaric acid, of *cis*- and *trans*-methylisopropylglutaric acids, and of  $\alpha\alpha\beta\beta$ -tetramethylglutaric acid were effected (Trans., 1901, 77, 939).

On applying this method to the preparation of the  $\alpha\beta$ -dimethylglutaric acids, we found that a good yield of the triethyl salt from which they can be derived, namely, ethyl  $\alpha$ -cyano- $\alpha\beta$ -dimethylglutarate,  $\text{CO}_2\text{Et}\cdot\text{CMe}(\text{CN})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , could be obtained by treating the sodium compound, derived by the condensation of ethyl sodiocyanoacetate and ethyl  $\beta$ -methylacrylate, with methyl iodide.

Our chief reason for desiring to prepare this ethyl salt was in order to study its behaviour on hydrolysis. We have already shown (Trans., 1900, 77, 928) that on hydrolysing those ethyl cyano-salts which should yield mixtures of *cis*- and *trans*-forms of alkylglutaric acids, a convenient method of separation lay in taking advantage of the ease with which, under certain conditions, the *cis*-acid amide passed into an imide insoluble in a dilute solution of sodium carbonate, leaving the *trans*-acid as acid amide or as *trans*-acid.

$\alpha\beta$ -Dimethylglutarimide, prepared in this way, melts at  $113^\circ$ , and, on hydrolysis with dilute sulphuric acid, gives *cis*- $\alpha\beta$ -dimethylglutaric acid, melting at  $87^\circ$ .

This acid is apparently identical with that prepared by Blaise, and described by him as melting at  $82$ — $83^\circ$ ; treated with acetyl chloride, it gives an anhydride boiling at  $255^\circ$  (765 mm.), which, on boiling with water, is reconverted into the *cis*-acid melting at  $87^\circ$ .

*trans*- $\alpha\beta$ -Dimethylglutaric acid is obtained from the sodium carbonate washings of the imide.

We have not been able to prepare this acid in a crystalline condition; repeated fractionation of the potassium salt from dilute alcohol failed to give any product which showed the slightest tendency to crystallise, and in fact, in whatever way the acid was prepared, it was always obtained as an oil.

On treatment with acetic anhydride, it is slowly converted into an anhydride, which, on boiling with water, is transformed into the *cis*-acid melting at  $87^\circ$ ; when the *trans*-acid is distilled, water is eliminated and an anhydride formed, which is identical with that prepared from the *cis*-acid with acetyl chloride.

The *cis*-acid, on heating in a sealed tube at  $180^\circ$  for 6 hours with hydrochloric acid, is partially converted into the *trans*-acid.



It seems strange that this substance should show so little tendency to crystallise, all the other members of this series being well-defined, crystalline solids. The acid is probably identical with that prepared by Montemartini, and described by him as a syrup.

If the methyl-alcoholic filtrate and washings from the potassium salt, mentioned on page 356, are evaporated to dryness and the residue boiled with water until ammonia has ceased to be evolved, an acid of the formula  $C_8H_{12}O_6$  is obtained on acidifying and extracting; this, which is evidently  $\alpha\beta$ -dimethylpropanetricarboxylic acid,



melts, with evolution of carbon dioxide, at  $168^\circ$ , being transformed into a mixture of *cis*- and *trans*- $\alpha\beta$ -dimethylglutaric acids; if distilled under the ordinary pressure, it is completely converted into the *cis*-anhydride boiling at  $255^\circ$ . The anilic acid prepared from this anhydride crystallises from dilute alcohol in lustrous plates and melts at  $149^\circ$ .

In connection with the method used by us for the separation of *cis*- and *trans*-forms of substituted glutaric acid, and which was only applicable to those acids which were derived from the hydrolysis of ethyl cyano-salts, we have now succeeded in devising a method which appears to be of general application.

The method consists in heating the mixed ammonium salts of the *cis*- and *trans*-acids at a high temperature in a sealed tube, whereby the *cis*-ammonium salt is converted into an imide, and the *trans*-ammonium salt remains unchanged.

It has already been frequently pointed out that the separation of *cis*- and *trans*-forms of these acids is a matter of some difficulty, and in order to test the efficacy of our method we have applied it, with satisfactory results, to mixtures of (1) *cis*- and *trans*- $\alpha\alpha'$ -dimethylglutaric acids, (2) *cis*- and *trans*- $\alpha$ -methyl- $\beta$ -isopropylglutaric acids, and (3) *cis*- and *trans*- $\alpha\alpha'\beta\beta$ -tetramethylglutaric acids.

In the first case, *cis*- $\alpha\alpha'$ -dimethylglutaric acid, melting at  $128^\circ$ , is readily separated from the product of hydrolysis, but the *trans*-modification, melting at  $141^\circ$ , is not so easily isolated (*Annalen*, 1895, 285, 272), and for a long time it was thought that an acid melting at  $103$ — $104^\circ$ , which, in reality, is an equimolecular mixture of the *cis*- and *trans*-forms, was the *trans*-modification of this acid.

We have now succeeded in separating these acids in the following way. The acid melting at  $103$ — $104^\circ$  was converted into the ammonium salt and heated in a sealed tube at  $160^\circ$  for 4 hours.

The product was found to consist of an imide and a quantity of unchanged ammonium salt. These were separated by means of ether, when the imide, which melted at  $176^\circ$ , gave, on hydrolysis, the pure

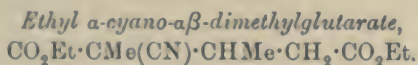


*cis*-acid melting at  $128^{\circ}$ , and the ammonium salt, on acidifying and extracting, yielded the pure *trans*-acid melting at  $141^{\circ}$ .

This method, which therefore appears to be of general application to acids of the glutaric series, is to be recommended, firstly, because the mixture of imide and ammonium salt can readily be separated by means of ether; secondly, because the imides are substances which can be readily purified by recrystallisation from water; and, thirdly, because although the *trans*-ammonium salt is gradually converted into the *cis*-imide on prolonged heating, yet the ammonium salt which remains is always the ammonium salt of the *trans*-acid, and always yields the pure acid on acidifying.

Care must be taken, however, that the temperature does not rise above  $180^{\circ}$ , as at  $200^{\circ}$  the *trans*-ammonium salt is slowly converted into the *cis*-imide, the change being usually complete on heating for 10 hours at  $250^{\circ}$ .

#### EXPERIMENTAL.



In preparing ethyl  $\beta$ -methylacrylate, we made use of the method adopted by us for producing similarly constituted  $\alpha\beta$ -unsaturated ethyl salts, namely, by boiling ethyl- $\alpha$ -bromo-*n*-butyrate with diethylaniline.

This reaction does not appear to have been previously investigated.

When the two substances are boiled together under the same conditions as yield ethyl  $\beta\beta$ -dimethylacrylate from ethyl  $\alpha$ -bromo*isovalerate* (Trans., 1889, 75, 48), that is, by dissolving the unchanged diethylaniline in hydrochloric acid and extracting the ethyl salt with ether, hardly any ethyl  $\beta$ -methylacrylate is produced, the product consisting almost entirely of substances of higher boiling point, the nature of which we hope, at some future time, to communicate to the Society.

If, however, the method described below is adopted, a yield of 35 per cent. of unsaturated ethyl salt is produced, and in spite of the poorness of this yield we found this to be the most satisfactory way of preparing this substance.

Fifty grams of ethyl  $\alpha$ -bromo-*n*-butyrate were boiled with 75 grams of diethylaniline for 2 hours, and the contents of the flask, which solidified on cooling, were mixed with ether and filtered from the diethylaniline hydrobromide which remained undissolved. The ether was then evaporated and the product fractionally distilled under the ordinary pressure.

Ethyl  $\beta$ -methylacrylate prepared in this way boils at  $138\text{--}140^{\circ}$ .

The condensation of this ethyl salt with ethyl sodiocyanoacetate

and the conversion of the product into its methyl derivative were then carried out as follows.

Ethyl cyanoacetate (113 grams) was added to the equivalent quantity (1 mol.) of sodium dissolved in alcohol, mixed with 114 grams of ethyl  $\beta$ -methylacrylate, and heated on the water-bath for 24 hours. Excess of methyl iodide was then added and the heating continued for 3 hours longer.

The excess of alcohol and methyl iodide was separated and the ethyl salt fractionally distilled under diminished pressure. The yield is 60 per cent. of that theoretically possible.

Ethyl  $\alpha$ -cyano- $\alpha\beta$ -dimethylglutarate boils at  $185^\circ$  (20 mm.):

0.1795 gave 0.3945  $\text{CO}_2$  and 0.1288  $\text{H}_2\text{O}$ .  $\text{C} = 59.93$ ;  $\text{H} = 7.91$ .

$\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C} = 59.75$ ;  $\text{H} = 7.88$  per cent.

*Hydrolysis.*—On mixing a cold solution of potassium hydroxide in absolute methyl alcohol with an equivalent quantity of this ethyl salt, a crystalline potassium salt slowly separated. This was collected, washed with methyl alcohol, and dried in a desiccator over sulphuric acid:

0.1931 gave 0.1276  $\text{K}_2\text{SO}_4$ .  $\text{K} = 29.67$ .

$\text{C}_8\text{H}_9\text{O}_4\text{NK}_2$  requires  $\text{K} = 29.88$  per cent.

It was evidently, therefore, the potassium salt of  $\alpha$ -cyano- $\alpha\beta$ -dimethylglutaric acid.

$\alpha$ -Cyano- $\alpha\beta$ -dimethylglutaric acid,  $\text{CO}_2\text{H} \cdot \text{CMe}(\text{CN}) \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared from this potassium salt by dissolving it in a little water, acidifying with hydrochloric acid, and extracting with ether, is a white solid, which separates from a mixture of ether and light petroleum (b. p.  $40$ — $60^\circ$ ) in microscopic needles, and melts at  $132$ — $133^\circ$ :

0.2152 gave 0.4005  $\text{CO}_2$  and 0.1227  $\text{H}_2\text{O}$ .  $\text{C} = 51.79$ ;  $\text{H} = 6.32$ .

$\text{C}_8\text{H}_{11}\text{O}_4\text{N}$  requires  $\text{C} = 51.89$ ;  $\text{H} = 5.95$  per cent.

$\alpha\beta$ -Dimethylglutarimide,  $\text{CHMe} \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ \text{CH}_2 - \text{CO} \end{smallmatrix} \text{NH}$ , is best prepared by boiling  $\alpha$ -cyano- $\alpha\beta$ -dimethylglutaric acid or its potassium salt with concentrated hydrochloric acid until carbon dioxide ceases to be evolved. The product is then diluted with water, extracted with ether, and the extract washed with dilute sodium carbonate solution. On evaporating the ether, the imide is obtained as a white, crystalline powder, which crystallises from water in long needles, and melts at  $113^\circ$ :

0.2176 gave 17.9 c.c. nitrogen at  $14^\circ$  and 755 mm.  $\text{N} = 9.72$ .

$\text{C}_7\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{N} = 9.93$  per cent.

The *silver* salt, prepared by adding silver nitrate to a solution of the

imide made slightly alkaline with ammonia, forms white, microscopic needles rapidly darkening on exposure to light :

0.1463 gave 0.0637 Ag.  $\text{Ag} = 43.54$ .

$\text{C}_7\text{H}_{10}\text{O}_2\text{NAg}$  requires  $\text{Ag} = 43.32$  per cent.

*cis- $\alpha\beta$ -Dimethylglutaric acid*,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .—The imide is best hydrolysed by boiling with a 30 per cent. solution of sulphuric acid for 2 hours, the product yielding the above acid on extraction with ether.

It crystallises from concentrated hydrochloric acid in needles and melts at  $87^\circ$  :

0.1643 gave 0.3154  $\text{CO}_2$  and 0.1143  $\text{H}_2\text{O}$ .  $\text{C} = 52.85$  ;  $\text{H} = 7.72$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$  ;  $\text{H} = 7.50$  per cent.

The *silver* salt is obtained as a white, amorphous precipitate on adding silver nitrate solution to a neutral solution of the ammonium salt :

0.3536 gave 0.2047 Ag.  $\text{Ag} = 57.89$ .

$\text{C}_7\text{H}_{10}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 57.75$  per cent.

The *anhydride* is rapidly formed when the *cis*-acid is warmed with excess of acetyl chloride, and remains as an oil insoluble in sodium carbonate solution on evaporating the solution. It distils at  $255^\circ$  (765 mm.) :

0.1023 gave 0.2232  $\text{CO}_2$  and 0.0675  $\text{H}_2\text{O}$ .  $\text{C} = 59.40$  ;  $\text{H} = 7.33$ .

$\text{C}_7\text{H}_{10}\text{O}_3$  requires  $\text{C} = 59.15$  ;  $\text{H} = 7.04$  per cent.

The anhydride slowly dissolves in boiling water, being converted into the *cis*-acid melting at  $87^\circ$ , which can be extracted from the solution by means of ether.

*trans- $\alpha\beta$ -Dimethylglutaric acid*,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .—As stated in the introduction, we have been unable to obtain this acid in a crystalline condition. It was obtained as a gum on extracting the sodium carbonate washings of the ether solution containing the imide (see above), and was purified by conversion into the copper salt, the salt being decomposed by means of hydrogen sulphide. The aqueous filtrate from the copper sulphide was evaporated as far as possible on the water-bath, dissolved in ether, the ethereal solution dried with calcium chloride, and the residue left on evaporation placed in a vacuum-desiccator over sulphuric acid for 3 days :

0.2354 gave 0.4561  $\text{CO}_2$  and 0.1579  $\text{H}_2\text{O}$ .  $\text{C} = 52.84$  ;  $\text{H} = 7.45$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$  ;  $\text{H} = 7.50$  per cent.

Amongst the many experiments tried in order to obtain this acid in a crystalline condition was the fractional precipitation of the potassium salt from alcohol, and in this way five fractions were obtained, from



each of which the same syrup was isolated, a similar result attending the conversion of the acid into its barium salt by adding barium hydroxide to an aqueous solution of the acid, saturating with carbon dioxide, filtering, and evaporating to a small bulk.

The *anilic acid*,  $\text{CHMe} \begin{smallmatrix} < \text{CHMe} \cdot \text{CONHPh} \\ \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$ ?, is prepared by adding a benzene solution of aniline to a benzene solution of the *cis*-anhydride, and separates from dilute alcohol in lustrous plates melting at  $149^\circ$ :

0.2130 gave 10.8 c.c. nitrogen at  $18^\circ$  and 764 mm.  $\text{N} = 5.8$ .

$\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{N} = 5.9$  per cent.

*$\alpha\beta$ -Dimethylpropanetricarboxylic acid*,



is obtained from the filtrate of the potassium salt (see page 356) on evaporating several times with water, acidifying, and extracting with ether; it crystallises from dilute hydrochloric acid in needles, and melts with decomposition at  $165^\circ$ :

0.2040 gave 0.3543  $\text{CO}_2$  and 0.1058  $\text{H}_2\text{O}$ .  $\text{C} = 47.35$ ;  $\text{H} = 5.76$ .

$\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C} = 47.29$ ;  $\text{H} = 5.41$ .

This tribasic acid, when heated at  $200^\circ$ , evolves carbon dioxide and is converted into a mixture of *cis*- and *trans*- $\alpha\beta$ -dimethylglutaric acids.

### *The Separation of cis- and trans-Forms of Substituted Glutaric Acids.*

#### *Separation of cis- and trans- $\alpha\alpha'$ -Dimethylglutaric Acids.*

As mentioned in the introduction, a number of mixtures of *cis*- and *trans*-forms of substituted glutaric acids were subjected to a treatment by which their mixed ammonium salts were heated in sealed tubes.

The first substance subjected to this treatment was the mixture of *cis*- and *trans*- $\alpha\alpha'$ -dimethylglutaric acids melting at  $102$ – $103^\circ$ , which was for a long time thought to be the *trans*-modification of the acid.

This mixture was converted into the ammonium salt and the dried salt heated in a sealed tube at  $160^\circ$  for 4 hours. The semi-liquid product was then treated with ether, it being usually found most convenient first to add water and then to extract the aqueous solution. The ethereal extract, on evaporation, gave a solid residue, which, after being once recrystallised from water, melted at  $173$ – $175^\circ$ :

0.1885 gave 16.4 c.c. nitrogen at  $17^\circ$  and 749 mm.  $\text{N} = 9.98$ .

$\text{C}_7\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{N} = 9.93$ .

It was evidently, therefore, the imide of  $\alpha\alpha'$ -dimethylglutaric acid, for on boiling with a 30 per cent. solution of sulphuric acid it was rapidly hydrolysed, and on extracting the product with ether, *cis*- $\alpha\alpha'$ -dimethylglutaric acid melting at  $128^\circ$  was obtained in almost theoretical quantities.

The aqueous solution, after extracting with ether, was acidified and again extracted, the ethereal extract yielding a solid on evaporation, which, after once recrystallising from water, melted at  $140$ — $141^\circ$  and evidently consisted of pure *trans*- $\alpha\alpha'$ -dimethylglutaric acid :

0.2073 gave 0.3976  $\text{CO}_2$  and 0.1380  $\text{H}_2\text{O}$ .  $\text{C} = 52.32$  ;  $\text{H} = 7.39$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$  ;  $\text{H} = 7.50$ .

#### *Separation of cis and trans- $\alpha\beta$ -Methylisopropylglutaric Acids.*

In this case, a mixture of the pure *cis*- and *trans*-acids in equal proportion was taken.

The ammonium salts were heated at  $160^\circ$  for 4 hours, the product dissolved in water, extracted with ether, and the residue left on evaporating the ether recrystallised from water, when it was found to melt at  $114$ — $115^\circ$ , evidently being the imide of  $\alpha$ -methyl- $\beta$ -isopropylglutaric acid previously described (Trans., 1900, '77, 946), since, on hydrolysis, it yielded the *cis*-acid melting at  $137^\circ$ . The *trans*-acid melting at  $101^\circ$  was obtained from the aqueous solution of the acidified ammonium salt.

The *cis*- and *trans*-acids recovered in this way were in about equal proportions, showing that under the conditions of the experiment very little *trans*-ammonium salt had been converted into *cis*-imide.

An experiment conducted at  $180^\circ$  for 10 hours gave the proportion of *cis* to *trans* as about 1 : 3, and one at  $200^\circ$  for 12 hours as about 1 : 5, showing that the increase of temperature and duration of heating rapidly converted the *trans*-ammonium salt into *cis*-imide.

#### *Separation of cis- and trans- $\alpha\alpha'\beta\beta$ -Tetramethylglutaric Acids.*

In this case, we experimented on the mixture of acids obtained from the ethyl salt derived from the condensation of ethyl sodiomethylcyanoacetate and ethyl dimethylacrylate (Trans., 1900, '77, 928).

These were converted into their ammonium salts in the usual way, and heated at  $160^\circ$  for 4 hours.

On working up the product in the manner previously described, an imide melting at  $108^\circ$  was obtained, and was found to be identical with the imide of  $\alpha\alpha'\beta\beta$ -tetramethylglutaric acid previously described (Trans., 1900, '77, 942), since, on hydrolysing with sulphuric acid, it yielded *cis*- $\alpha\alpha'\beta\beta$ -tetramethylglutaric acid, melting at  $140^\circ$ .

*trans-αα'ββ*-Tetramethylglutaric acid, melting at 98°, was obtained on extracting the acidified solution of the ammonium salt after the extraction of the imide with ether.

This method appears, then, to be of general application to acids of the glutaric series, and seems to yield the *cis*- and *trans*- forms of these acids in about the same proportion in which they exist in the mixture.

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### XXXIX.—*The Condensation of Phenyl Ethyl Ketone (Propiophenone) with Benzylideneacetophenone and of Acetophenone with Benzylidenepropiophenone.*

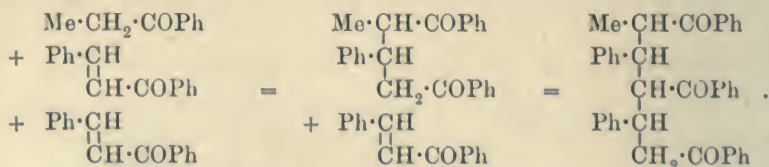
By ROBERT DUNCOMBE ABELL, Ph.D. (Leipzig), B.Sc. (Wales), 1851 Exhibition Scholar of the University College of North Wales, Bangor.

UNDER the condensing influence of sodium ethoxide, phenyl ethyl ketone unites with benzylideneacetophenone in two proportions yielding:

i. 1 : 3-Dibenzoyl-2-phenyl-1-methylpropane,



ii. 1 : 3 : 5-Tribenzoyl-2 : 4-diphenyl-1-methylpentane, the production of which may be regarded as being due to the union of 1 mol. of 1 : 3-dibenzoyl-2-phenyl-1-methylpropane with 1 mol. of benzylideneacetophenone :



It is conceivable that this triketone might again unite with a molecule of benzylideneacetophenone, but so far the formation of such tetraketones has not been observed.

The condensation of phenyl ethyl ketone with benzylideneacetophenone takes place almost entirely in the manner indicated.

The diketone, 1 : 3-dibenzoyl-2-phenyl-1-methylpropane, reacts with hydroxylamine to form a dioxime,  $\text{C}_{24}\text{H}_{24}\text{O}_3\text{N}_2$ , and with hydroxylamine



hydrochloride to give [rise to] 2 : 4 : 6-triphenyl-3-methylpyridine,  $C_{24}H_{19}N$ .

Acetophenone and benzylidenepropiophenone should also condense in molecular proportions to give the same or a stereoisomeric 1 : 3-dibenzoyl-2-phenyl-1-methylpropane.

Further, 1 mol. of acetophenone should condense with 2 mols. of benzylidenepropiophenone to form 1 : 3 : 5-tribenzoyl-2 : 4-diphenyl-1 : 5-dimethylpentane,



the formation of which may also take place by the condensation of 1 mol. of 1 : 3-dibenzoyl-2-phenyl-1-methylpropane with 1 mol. of benzylidenepropiophenone.

The condensation of acetophenone with benzylidenepropiophenone does not, however, take place as represented above.

When sodium ethoxide (20 per cent. solution) was used as condensing reagent, the following substances were obtained: (i) 1 : 3-dibenzoyl-2-phenyl-1 : 3-dimethylpropane,  $C_{23}H_{24}O_2$ , m. p. 162—163°, six-sided crystals (Trans., 1901, 79, 936); (ii) prisms, m. p. 93—94°, a mixture of two homologous 1 : 5-diketones, namely, 1 : 3-dibenzoyl-2-phenylpropane and 1 : 3-dibenzoyl-2-phenyl-1-methylpropane, which could not be separated by crystallisation, but which were identified by means of the corresponding dioximes and pyridines; (iii) 1 : 3-dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ , prisms, m. p. 103·5—104·5°; (iv) 1 : 3 : 5-tribenzoyl-2 : 4-diphenyl-1-methylpentane,  $C_{39}H_{34}O_3$ , rhombic plates, m. p. 241—242°; (v) 1 : 3 : 5-tribenzoyl-2 : 4-diphenylpentane,  $C_{38}H_{32}O_3$ , acicular, glistening prisms aggregated in rosettes, m. p. 255—256° (Kostanecki and Roszbach, *Ber.*, 1896, 29, 1492); (vi) benzoic acid in very small quantity, which was separated by distillation with steam from (vii) a pink-coloured, viscid, acid liquid, which is formed in too small a quantity to investigate.

In this condensation the first separation of oil or crystals only takes place after some days, and even after 14 days some unchanged substance remained, whilst a quantity of resin was always formed along with the other products of the reaction.

The condensation is consequently not so direct as that which takes place between phenyl ethyl ketone and benzylideneacetophenone, and this appears to be due to the ease with which benzylidenepropiophenone is decomposed into phenyl ethyl ketone and benzaldehyde by means of sodium ethoxide.\* This fact, combined with the knowledge that benzylideneacetophenone is decomposed by alkalis (Kostanecki and Tambor, *Ber.*, 1896, 29, 1425), explains the formation of the above-named substances.

After the mixture has stood for a short time the benzylidenepropio-

\* The author hopes shortly to communicate a paper on this subject.

phenone is decomposed in part to phenyl ethyl ketone and benzaldehyde, consequently condensation occurs between acetophenone, benzylidenepropiophenone, phenyl ethyl ketone, and benzaldehyde, so as to give the substances which have been isolated. A small portion of the benzaldehyde is oxidised to benzoic acid, whilst the formation of the unknown acid and the resin is due to a more obscure reaction.

Under the influence of sodium ethoxide suspended in dry ether, the condensation of acetophenone and benzylidenepropiophenone follows much the same course as in alcoholic solution. A larger quantity of resin is, however, formed.

With an alcoholic solution of sodium hydroxide the following substances were isolated : (i) 1 : 3-dibenzoyl-2-phenyl-1 : 3-dimethylpropane,  $C_{25}H_{24}O_2$ , six-sided crystals, m. p.  $162-163^\circ$ ; (ii) the mixture of the homologous diketones, 1 : 3-dibenzoyl-2-phenylpropane,  $C_{23}H_{20}O_2$ , and 1 : 3-dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ ; (iii) unchanged acetophenone and benzylidenepropiophenone.

*Condensation of Phenyl Ethyl Ketone with Benzylideneacetophenone.*

A solution of 0.95 gram of sodium in 20 c.c. of absolute alcohol was added to 5.4 grams of phenyl ethyl ketone and 8.4 grams of benzylideneacetophenone in 30 c.c. of the same solvent. The mixture, which at once assumed a pink colour with evolution of heat, yielded drops of oil which rapidly became crystalline, and within an hour the whole had become a thick, crystalline sludge. After 4 days, the crystals were collected, washed with 50 per cent. alcohol, and finally with water, the filtrate being precipitated with water and extracted with ether. This ethereal solution, on evaporation, gave a further quantity of crystals along with a small amount of oil.

The products of the reaction were boiled with alcohol and gave :

i. 1 : 3 : 5-Tribenzoyl-2 : 4-diphenyl-1-methylpentane, an almost insoluble, finely crystalline residue, which separates from dilute acetone in rhombic plates melting at  $241-242^\circ$  :

0.2005 gave 0.6245  $CO_2$  and 0.1134  $H_2O$ . C = 84.94 ; H = 6.28.

0.2002 „ 0.6235  $CO_2$  „ 0.1125  $H_2O$ . C = 84.93 ; H = 6.24.

$C_{39}H_{34}O_3$  requires C = 85.09 ; H = 6.18 per cent.

It is almost insoluble in boiling absolute alcohol, or ligroin, easily soluble in acetone, and dissolves in pure concentrated sulphuric acid to a yellow solution which on standing assumes a dull red colour.

ii. 1 : 3-Dibenzoyl-2-phenyl-1-methylpropane (prisms, m. p.  $103.5-104.5^\circ$ ) is readily soluble in boiling alcohol, or acetone, sparingly so in cold alcohol, or ligroin (b. p.  $80-85^\circ$ ), and dissolves in

pure concentrated sulphuric acid to a pale yellow solution which darkens on standing :

0.2010 gave 0.6195  $\text{CO}_2$  and 0.1195  $\text{H}_2\text{O}$ .  $\text{C} = 84.05$  ;  $\text{H} = 6.60$ .  
 0.2005 „ 0.6182  $\text{CO}_2$  „ 0.1187  $\text{H}_2\text{O}$ .  $\text{C} = 84.08$  ;  $\text{H} = 6.58$ .  
 $\text{C}_{24}\text{H}_{22}\text{O}_2$  requires  $\text{C} = 84.21$  ;  $\text{H} = 6.43$  per cent.

*Action of Hydroxylamine on Dibenzoylphenylmethylpropane*  
 (m. p. 103.5—104.5°).

The diketone, when boiled for 3 hours with 4 mols. of free hydroxylamine in alcoholic solution, gave an oil the greater part of which became crystalline on the addition of chloroform. The oil, which is probably the monoxime, is easily soluble in chloroform, but does not crystallise. When heated with a further quantity of free hydroxylamine, it was almost completely converted into the crystalline compound. This substance, which is sparingly soluble in chloroform, crystallises from dilute acetone in needles melting at 204—205° :

0.2010 gave 0.5705  $\text{CO}_2$  and 0.1200  $\text{H}_2\text{O}$ .  $\text{C} = 77.41$  ;  $\text{H} = 6.60$ .  
 0.2370 gave 15.7 c.c. nitrogen at 16° and 758 mm.  $\text{N} = 7.70$ .  
 $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2$  requires  $\text{C} = 77.42$  ;  $\text{H} = 6.45$  ;  $\text{N} = 7.52$  per cent.

This dioxime is insoluble in sodium hydroxide, or ligroin, and moderately soluble in benzene, alcohol, or acetone.

*Action of Hydroxylamine Hydrochloride on Dibenzoylphenylmethylpropane* (m. p. 103.5—104.5°).

Two grams of the diketone, 1 gram of hydroxylamine hydrochloride, and 15 c.c. of 90 per cent. alcohol were heated in a sealed tube at 120—130° for 4 hours. The contents of the tube were precipitated with water and extracted with ether. The ethereal solution left, on evaporation, a pink, crystalline mass, which, after many crystallisations from alcohol, separated in colourless prisms melting at 141—142° :

0.2030 gave 0.6675  $\text{CO}_2$  and 0.1110  $\text{H}_2\text{O}$ .  $\text{C} = 89.67$  ;  $\text{H} = 6.07$ .  
 0.2000 „ 8.7 c.c. nitrogen at 24.5° and 762 mm.  $\text{N} = 4.63$ .  
 2 : 4 : 6-Triphenyl-3-methylpyridine,  $\text{C}_{24}\text{H}_{19}\text{N}$ , requires  $\text{C} = 89.72$  ;  
 $\text{H} = 5.92$  ;  $\text{N} = 4.36$  per cent.

When a solution of this substance in hot alcohol was added to an alcoholic solution of an equal quantity of picric acid, a sparingly soluble picrate, which crystallised in yellow prisms (m. p. 190—191°), separated on cooling :

0.2000 gave 19 c.c. nitrogen at 24° and 758 mm.  $\text{N} = 10.62$ .  
 $\text{C}_{24}\text{H}_{19}\text{N}, \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$  requires  $\text{N} = 10.48$  per cent.



Triphenylmethylpyridine is soluble in concentrated hydrochloric acid, and is reprecipitated by alkalis. When a current of dry hydrogen chloride is passed into a solution of triphenylmethylpyridine in pure dry ether, the hydrochloride separates as a crystalline powder, which is extremely hygroscopic and cannot be exposed even momentarily without undergoing superficial decomposition.

*Condensation of Acetophenone and Benzylidenepropiophenone.*

A solution of 1 gram of sodium in 16 grams of absolute alcohol was added to a mixture of 4.8 grams of acetophenone and 8.8 grams of benzylidenepropiophenone. After standing for 4 days, the deep red solution yielded a viscid, red oil, which subsequently became partly crystalline. In the different experiments the mixture was allowed to remain for periods ranging from 4 to 14 days, but the product, when dissolved in ether and water, yielded an ethereal solution containing the substances enumerated on p. 361.

The aqueous solution, when acidified with hydrochloric acid, was extracted with ether. The ethereal solution yielded benzoic acid and a very viscid, red oil having an acid reaction, the amount of which was too small to admit of further investigation.

*Investigation of the Substances obtained in the preceding Condensation.*

i. The six-sided crystals melting at  $162-163^{\circ}$  were identified as 1:3-dibenzoyl-2-phenyl-1:3-dimethylpropane,  $C_{25}H_{24}O_2$ , also obtained by the condensation of phenyl ethyl ketone with benzylidenepropiophenone (Trans., 1901, 79, 936).

ii. The colourless prisms (m. p.  $93-94^{\circ}$ ) were readily soluble in benzene, chloroform, methyl alcohol, acetone, carbon bisulphide, ether, acetic acid, or toluene, less so in ethyl alcohol and petroleum of high boiling point, and dissolved sparingly in light petroleum or ligroin. They were recrystallised from both alcohol and ligroin:

0.2002 gave 0.6172  $CO_2$  and 0.1135  $H_2O$ .  $C = 84.07$ ;  $H = 6.29$ .

0.2010 „ 0.6204  $CO_2$  „ 0.1151  $H_2O$ .  $C = 84.17$ ;  $H = 6.36$ .

1:3-Dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ , requires  $C = 84.21$ ;  $H = 6.43$  per cent.

1:3-Dibenzoyl-2-phenylpropane,  $C_{23}H_{20}O_2$ , requires  $C = 84.14$ ;  $H = 6.10$ . Mean:  $C = 84.17$ ;  $H = 6.26$  per cent.

The analyses of this substance gave results which do not agree with those required by either of the pure diketones, but agree quite well with the numbers which would be required by a mixture of equal quantities of these compounds. It is worthy of note that the melting point  $93-94^{\circ}$  is the mean of the melting points of dibenzoylphenyl-

methylpropane, m. p. 103·5—104·5°, and of dibenzoylphenylpropane, m. p. 85—86°.

A molecular weight determination, in which 0·3245 gram of the substance dissolved in 29·34 grams of chloroform produced a rise of 0·127° in the boiling point, gave a molecular weight of 335 :

$$C_{24}H_{22}O_2 = 342 ; C_{23}H_{20}O_2 = 328. \quad \text{Mean} = 335.$$

All the evidence pointed to the substance being a mixture of the two homologous 1:5-diketones. This view was confirmed by its behaviour towards free hydroxylamine and hydroxylamine hydrochloride. It was also found that the substance melting at 93—94° could be prepared by crystallising equal quantities of the pure diketones from alcohol or ligroin ; the substance obtained could not again be separated into its constituents by recrystallisation from any of the above solvents. Between what limits the substances are miscible has not yet been determined ; it was found, however, that a mixture of 3 parts of dibenzoylphenylpropane with 1 part of dibenzoylphenylmethylpropane crystallised as a simple substance from alcohol and from ligroin and melted at 93—94°, but a mixture of 1 part of dibenzoylphenylpropane with 3 parts of dibenzoylphenylmethylpropane did not remain homogeneous upon recrystallisation, but could be separated into two parts, the one consisting of pure dibenzoylphenylmethylpropane, m. p. 103·5—104·5°, the other consisting of the mixed ketones, m. p. 93—94°.

*Action of Hydroxylamine on the Substance (m. p. 93—94°).*—Two grams of the substance were added to an aqueous alcoholic solution of 2 grams of hydroxylamine hydrochloride and 2·4 grams of sodium acetate, and heated to boiling for 3 hours. The product was evaporated and the residue dissolved in ether and water. The crystalline substance, which remained after the evaporation of the ether, was recrystallised from benzene, and gave (i) disc-shaped, highly refractive crystals (m. p. 186—187°); this substance crystallised from dilute acetone in needles melting at 204—205°, and was identified as the dioxime of 1:3-dibenzoyl-2-phenyl-1-methylpropane (see p. 363).

(ii) White needles aggregated in small clusters, which, when crystallised from a mixture of benzene and ligroin, separated in small, white needles, m. p. 163—164°. This substance agrees in composition and properties with the dioxime of 1:3-dibenzoyl-2-phenylpropane described by Wislicenus and Newman (*Annalen*, 1898, 302, 236).

*Action of Hydroxylamine Hydrochloride on the Substance (m. p. 93—94°).*—Two grams of the substance, 1 gram of hydroxylamine hydrochloride, and 15 c.c. of 90 per cent. alcohol were heated in a sealed tube at 120—130° for 4 hours, the pink-coloured needles so obtained were recrystallised from ligroin, and gave (i) clusters of dark yellow plates ; (ii) colourless prisms. These products had

to be separated mechanically, and then crystallised from ligroin until the melting points become constant. Each substance still requires to be recrystallised a number of times from alcohol.

The yellow plates ultimately gave long, colourless needles (m. p. 137—138°), which dissolve in pure concentrated sulphuric acid with a deep blue fluorescence. This substance agrees with the 2:4:6-triphenylpyridine,  $C_{23}H_{17}N$ , described by Wislicenus and Newman (*Annalen*, 1898, 302, 236).

The colourless prisms, after many crystallisations from alcohol, melt at 141—142°. This substance being thus identified as 2:4:6-triphenyl-3-methylpyridine (p. 363).

The substance, m. p. 93—94°, is therefore a mixture of two homologous 1:5-diketones, 1:3-dibenzoyl-2-phenylpropane,  $C_{23}H_{20}O_2$ , and 1:3-dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ ; the quantity of the former being about twice that of the latter, as ascertained from a comparison of the yields of the dioximes and of the pyridines.

iii. The prisms (m. p. 103·5—104·5°) were obtained in very small quantity:

0·201 gave 0·6204  $CO_2$  and 0·1198  $H_2O$ .  $C = 84·17$ ;  $H = 6·62$ .

1:3-dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ , requires  $C = 84·21$ ;  $H = 6·43$  per cent.

iv. The rhombic plates (m. p. 241—242°) agree in properties with 1:3:5-tribenzoyl-2:4-diphenyl-1-methylpentane (p. 362), but the quantity of this substance obtained was too small for analysis.

v. The glistening prisms (m. p. 255—256°) were also isolated in very small quantities. The substance was not analysed, but characterised by means of its additive compounds with benzene and with toluene, determinations of these being used as a means of identification.

Benzene of crystallisation: 0·0538 lost 0·0068 benzene on heating at 130°. Benzene = 12·6.  $C_{38}H_{32}O_3, C_6H_6$  requires benzene = 12·7 per cent.

Toluene of crystallisation: 0·054 lost 0·0078 toluene on heating at 130°. Toluene = 14·44.  $C_{38}H_{32}O_3, C_7H_8$  requires toluene = 14·6 per cent.

This substance is soluble in pure concentrated sulphuric acid to a magenta-red solution with a yellowish-red fluorescence, which disappears on standing.

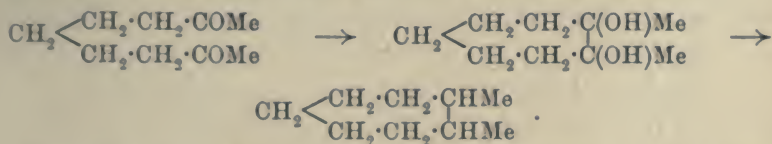
The substance agrees with the dibenzylidenetriacetophenone or 1:3:5-tribenzoyl-2:4-diphenylpentane described by Kostanecki and Rossbach (*Ber.*, 1896, 29, 1492).



**XL.—A Synthesis of 1 : 3 : 5-Triphenyl-2 : 4-dimethylcyclopentane and of 1 : 3 : 5-Triphenyl-2-methylcyclopentane.**

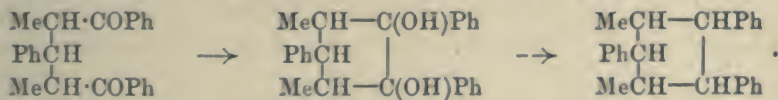
By ROBERT DUNCOMBE ABELL, Ph.D. (Leipzig), B.Sc. (Wales), 1851  
Exhibition Scholar of the University College of North Wales,  
Bangor.

PERKIN AND KIPPING (Trans., 1889, 55, 320) showed theoretically that it was possible to convert all diketones into carbocyclic compounds by reduction, and that the closing of the ring was due to the formation of cyclic pinacones, which may then be reduced to the hydrocarbons. Shortly afterwards, these chemists (Trans., 1891, 59, 215) obtained dimethylheptamethylene from  $\omega\omega$ -diacetylpentane through the intermediate cyclic pinacone, dihydroxydimethylheptamethylene,



Since that time J. Wislicenus (*Ber.*, 1895, 28, 2102; *Annalen*, 1898, 302, 215) has applied this reaction with great success to the preparation of *cyclopentane* derivatives from 1 : 5-diketones.

In accordance with the above, the 1 : 5-diketone, 1 : 3-dibenzoyl-2-phenyl-1 : 3-dimethylpropane,  $\text{C}_{25}\text{H}_{24}\text{O}_2$  (m. p. 162—163°) (Trans, 1901, 79, 928), when reduced with zinc dust and acetic acid, gave the cyclic pinacone, triphenyldimethyl*cyclopentane*diol,  $\text{C}_{25}\text{H}_{26}\text{O}_2$ ; this product was further reduced by a mixture of red phosphorus and hydriodic acid, whereby two substances were obtained which were identified as stereoisomeric triphenyldimethyl*cyclopentanes*,  $\text{C}_{25}\text{H}_{26}$ .

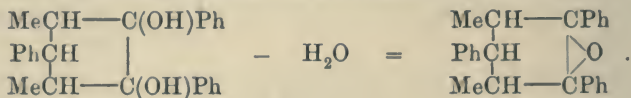


The possibility of the existence of such isomerides depends on the relative position of the various groups with respect to the plane of the *cyclopentane* ring.

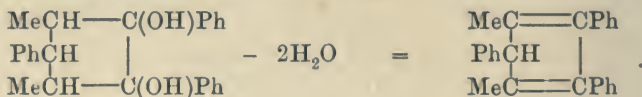
The pinacone readily loses 2 molecules of water when it is heated with fused oxalic acid, to form an unsaturated hydrocarbon triphenyldimethyl*cyclopentadiene*,  $\text{C}_{25}\text{H}_{22}$ . This behaviour depends upon the relative positions of the hydroxyl groups and the hydrogen atoms attached to adjacent carbon atoms of the *cyclopentane* ring with respect to the plane of the ring.

There are three possible positions :

(i) If the hydroxyl groups are on one side, and the hydrogen atoms, which are attached to the adjacent carbon atoms, on the opposite side of the plane of the ring, then the pinacone may, by the action of the acids, lose 1 molecule of water to form a pinacoline in the following manner (Wislicenus and Lehmann, *Annalen*, 1898, 302, 207) :



(ii) If the hydroxyl groups are one on each side of the plane of the ring, and the hydrogen atom attached to the adjacent carbon atom is in each case on the *same* side of the hydroxyl group, then 2 molecules of water may be split away by the action of dehydrating agents with the formation of a doubly unsaturated hydrocarbon (Wislicenus and Carpenter, *Annalen*, 1898, 302, 223). Thus the pinacone would give triphenyldimethylcyclopentadiene :



(iii) If the hydroxyl groups are one on each side of the plane of the ring, and the hydrogen atom attached to the adjacent carbon atom is in each case on the *opposite* side with respect to the hydroxyl group, then no separation of water can take place, or only with great difficulty.

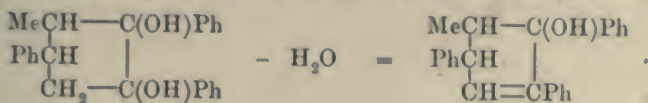
The behaviour of the pinacone towards oxalic acid corresponds with the second formula. Although the hydrocarbon is doubly unsaturated, it does not take up bromine. However, it gives the characteristic pentadiene reaction, and on reduction yields the saturated hydrocarbon triphenyldimethylcyclopentane.

Similarly, the reduction of 1 : 3-dibenzoyl-2-phenyl-1-methylpropane,  $\text{C}_{24}\text{H}_{22}\text{O}_2$ , by sodium amalgam gives triphenylmethylocyclopentenediol,  $\text{C}_{24}\text{H}_{24}\text{O}_2$ , which is reduced by red phosphorus and hydriodic acid to two stereoisomeric triphenylmethylocyclopentanes,  $\text{C}_{24}\text{H}_{24}$ ; the one crystallising in needles (m. p. 121—122°), the other being a straw-yellow oil (b. p. 260—262°, 28 mm.).

The pinacone splits off water more readily than the next higher homologue, so that when the 1 : 5-diketone is reduced by zinc dust and acetic acid, a quantity of the pinacone loses two molecules of water to form the unsaturated hydrocarbon, triphenylmethylocyclopentadiene,  $\text{C}_{24}\text{H}_{20}$ , which may be obtained in greater quantity by heating the pinacone with fused oxalic acid.

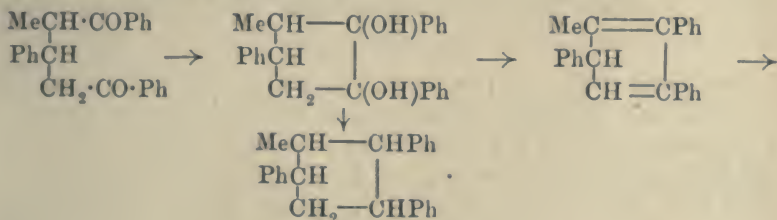
The separation of water from triphenylmethylocyclopentenediol may

take place as indicated by (i) and (ii) on p. 368. The third possibility, however, cannot apply in the present instance, because in this case one of the hydroxyl groups is always so situated as to be on the same side of the plane of the ring as a hydrogen atom which is attached to the adjacent carbon atom, and consequently a molecule of water may split off to form 1-hydroxy-1 : 3 : 5-triphenyl-2-methyl- $\Delta^4$ -cyclopentene :



The unsaturated hydrocarbon triphenylmethylcyclopentadiene is reduced by red phosphorus and hydriodic acid to the stereoisomeric triphenylmethylcyclopentanes.

The relation between the diketone and its reduction products is shown by the following formulæ :



*Reduction of 1 : 3-Dibenzoyl-2-phenyl-1 : 3-dimethylpropane,  $\text{C}_{25}\text{H}_{24}\text{O}_2$ , m. p. 162—163°.*

A solution of 4 grams of the diketone in 100 grams of 85 per cent. acetic acid with 6 grams of zinc dust was boiled continuously for 8 hours under a reflux condenser. The hot straw-yellow solution was poured into a litre of water and allowed to stand for 12 hours. The precipitate crystallises from ligroin (b. p. 80—85°) in colourless prisms melting at 143—144°.

0.2165 gave 0.6650  $\text{CO}_2$  and 0.1447  $\text{H}_2\text{O}$ . C = 83.77; H = 7.42.

0.2012, „ 0.6175  $\text{CO}_2$  „ 0.1330  $\text{H}_2\text{O}$ . C = 83.70; H = 7.34.

$\text{C}_{25}\text{H}_{26}\text{O}_2$  requires C = 83.79; H = 7.27 per cent.

If, during the reduction, the boiling be interrupted for more than a few minutes, the solution assumes a dark-brown colour, and one of the products of the reaction is a yellowish-brown, disagreeably smelling oil which decomposes on standing. If, however, the boiling is continuous, the solution remains almost colourless, and the yield of pinacone is 99—100 per cent. of the calculated quantity.

The pinacone is readily soluble in alcohol, ether, or acetic acid, but sparingly so in ligroin.



From the mother liquors, a minute quantity of a brownish-yellow substance was isolated, which, by repeated crystallisation from alcohol, was obtained in yellow, feathery needles melting at 126—127°.

0.1600 gave 0.548 CO<sub>2</sub> and 0.0985 H<sub>2</sub>O. C = 93.40; H = 6.83.

C<sub>25</sub>H<sub>22</sub> requires C = 93.17; H = 6.82 per cent.

This substance is the unsaturated hydrocarbon, triphenyldimethylcyclopentadiene (p. 368), formed from the pinacone by the dehydrating action of the acetic acid.

The solution of this compound cannot be decolorised by boiling with animal charcoal; a yellow alcoholic solution became dark red on boiling for 10 minutes with animal charcoal, and a quantity of the substance was changed to a dark, viscid oil, which could not be made to crystallise.

*Fusion of Triphenyldimethylcyclopentenediol with Anhydrous Oxalic Acid.*

Oxalic acid (100 grams) was heated in a hard glass flask, immersed in an oil-bath, until a thermometer, placed in the molten acid, showed a temperature of 138°; 3 grams of the pinacone were then added, and the flask heated strongly with a free flame until the contents suddenly solidified. Dilute alcohol was added to the cold porous product, and a sparingly soluble, flocculent mass remained undissolved, which crystallised from alcohol in clusters of white, feathery needles, m. p. 127—128°.

0.16 gave 0.5462 CO<sub>2</sub> and 0.0997 H<sub>2</sub>O. C = 93.10; H = 6.92.

C<sub>25</sub>H<sub>22</sub> requires C = 93.17; H = 6.82 per cent.

This hydrocarbon is identical with that obtained from the mother liquors of the pinacone, and is formed from the latter by the loss of 2 molecules of water (p. 368).

Being an unsaturated substance, it should take up 4 atoms of bromine. When, however, a solution of bromine in chloroform is added to a solution of the hydrocarbon, a copious evolution of hydrobromic acid takes place, with formation of a black, viscid oil, which afterwards solidifies. This substance dissolves readily in all the ordinary solvents, and separates from them as a black oil, which again solidifies after a while but remains amorphous.

The hydrocarbon is soluble in pure concentrated sulphuric acid to a yellow solution which subsequently develops an "eosin" fluorescence (pentadiene reaction).

*Reduction of Triphenyldimethylcyclopentanediol.*

A mixture of 3 grams of pinacone, 1.5 grams of red phosphorus, and 10 grams of hydriodic acid (sp. gr. 1.7) was heated for 7 hours at 190—200° in a sealed tube in which the air had been replaced by carbon dioxide. The contents of the tube were dissolved in ether and water and yielded an ethereal solution which, when washed with a dilute solution of sulphurous acid, then with water, and finally dried by means of fused sodium sulphate, left on evaporation in a current of dry air, a clear, colourless oil which became for the most part crystalline; the solid portion being dried on porous plates. The crystals separated from alcohol in needles (m. p. 80—81°):

0.2032 gave 0.6865 CO<sub>2</sub> and 0.1482 H<sub>2</sub>O. C = 92.13; H = 8.09.

0.1687 „ 0.5695 CO<sub>2</sub> „ 0.1205 H<sub>2</sub>O. C = 92.06; H = 7.94.

C<sub>25</sub>H<sub>26</sub> requires C = 92.03; H = 7.96 per cent.

The straw-yellow oil extracted from the porous plate distilled at 246—248° (25 mm.):

0.2022 gave 0.7147 CO<sub>2</sub> and 0.1557 H<sub>2</sub>O. C = 91.84; H = 8.15.

C<sub>25</sub>H<sub>26</sub> requires C = 92.03; H = 7.96 per cent.

Molecular weight determinations of these substances indicate that they are isomeric triphenyldimethylcyclopentanes:

|  | Needles,<br>m. p. 80—81°. | Oil, b. p. 246—248°<br>(25 mm.). |
|--|---------------------------|----------------------------------|
| Weight of substance.....               | 0.454                     | 0.692                            |
| „ solvent (chloroform) .....           | 28.88                     | 27.96                            |
| Observed rise of the boiling point ... | 0.168°                    | 0.28°                            |
| Molecular weight .....                 | 342                       | 323                              |
| C <sub>25</sub> H <sub>26</sub> = 326. |                           |                                  |

The crystalline form is the more stable of the two; the oily modification slowly becomes crystalline, the crystals being identical with those melting at 80—81°.

*Reduction of Triphenyldimethylcyclopentadiene.*

A mixture of 1 gram of the unsaturated hydrocarbon, 0.7 gram of red phosphorus, and 6 grams of hydriodic acid was heated for 8 hours at 200° in a sealed tube, and treated as above. The ethereal solution gave, on evaporation, a crystalline substance and a small amount of oil. The former crystallised from alcohol in needles (m. p. 80—81°):

0.2017 gave 0.68 CO<sub>2</sub> and 0.1487 H<sub>2</sub>O. C = 91.93; H = 8.19.

Triphenyldimethylcyclopentane, C<sub>25</sub>H<sub>26</sub>, requires C = 92.03; H = 7.96 per cent.

*Reduction of 1 : 3-Dibenzoyl-2-phenyl-1-methylpropane,  $C_{24}H_{22}O_2$ ,  
by Zinc Dust and Acetic Acid.*

Four grams of the diketone were dissolved in 100 grams of 85 per cent. acetic acid, 8 grams of zinc dust added, and the mixture heated to boiling for 8 hours. The yellow solution was poured into a litre of water. The white, flocculent, semi-crystalline precipitate crystallised from alcohol in long, yellow, flattened needles, m. p. 162—163°. These must be recrystallised a number of times from acetone in order to obtain a pure product :

0.2 gave 0.6845  $CO_2$  and 0.12  $H_2O$ . C = 93.34 ; H = 6.65.

$C_{24}H_{20}$  requires C = 93.51 ; H = 6.49 per cent.

This substance is the unsaturated hydrocarbon, triphenylmethylcyclopentadiene, formed from the pinacone by the dehydrating action of the acetic acid.

The alcoholic mother liquors gave, on evaporation, a brownish-yellow oil which partly crystallised on long standing, but which could not be recrystallised, as it separated from all solvents as an oil. It was subsequently found that the pinacone is an oil becoming crystalline with difficulty, and from analogy it was inferred that the above oil was impure pinacone. This was borne out by its behaviour towards fused oxalic acid, whereby a good yield of triphenylmethylcyclopentadiene was obtained.

*Reduction of 1 : 3-Dibenzoyl-2-phenyl-1-methylpropane by Sodium Amalgam.*

Two grams of the diketone were dissolved in moist ether, 50 grams of 3 per cent. sodium amalgam were added in small quantities at a time during 8 hours, and a rapid current of carbon dioxide was passed through the solution, which was kept constantly stirred. The washed and dried ethereal solution, which was evaporated in a stream of dry air, yielded a very viscid, colourless oil, which, when left in a vacuum-desiccator over sulphuric acid, crystallised in needles. This substance is readily soluble in all the organic solvents, and separates from them as an oil which again slowly crystallises ; it melts at 68—80° :

0.2017 gave 0.6167  $CO_2$  and 0.1315  $H_2O$ . C = 83.39 ; H = 7.24.

0.2012 „ 0.6155  $CO_2$  „ 0.131  $H_2O$ . C = 83.42 ; H = 7.20.

Triphenylmethylcyclopentanediol,  $C_{24}H_{24}O_2$ , requires C = 83.72 ; H = 6.97 per cent.

1 : 5-Dihydroxy-1 : 3 : 5-triphenyl-2-methylpentane,  $C_{24}H_{26}O_2$ , requires C = 83.24 ; H = 7.51 per cent.

The substance is therefore slightly impure pinacone, and not the dissecondary alcohol corresponding with the diketone.



*Behaviour of Triphenylmethylecyclopentanediol,  $C_{24}H_{24}O_2$ , towards Fused Oxalic Acid.*

Three grams of the pinacone were heated with fused oxalic acid (p. 367). On adding dilute alcohol to the cold, porous mass, a yellow, flocculent precipitate remained which crystallised from acetone in flattened, yellow needles melting at  $162-163^\circ$ :

0.2005 gave 0.6865  $CO_2$  and 0.1215  $H_2O$ .  $C = 93.37$ ;  $H = 6.73$ .

0.2015 „ 0.69  $CO_2$  „ 0.1225  $H_2O$ .  $C = 93.39$ ;  $H = 6.75$ .

$C_{24}H_{20}$  requires  $C = 93.51$ ;  $H = 6.49$  per cent.

Triphenylmethylecyclopentadiene is very sparingly soluble in alcohol and more so in acetone. It dissolves in pure concentrated sulphuric acid to a yellow solution which subsequently shows an "eosin" fluorescence.

The addition of a solution of bromine in chloroform to a solution of the hydrocarbon is followed by evolution of hydrobromic acid and formation of a yellowish-red oil.

*Reduction of Triphenylmethylecyclopentanediol.*

A mixture of 3 grams of pinacone, 1.5 grams of red phosphorus, and 10 grams of hydriodic acid (sp. gr. 1.7) was heated in a sealed tube at  $190^\circ$  for 5 hours. After treating the product in the usual manner, the dried ethereal solution gave, on evaporation, a colourless oil which became partly crystalline when left in a vacuum over sulphuric acid. The crystals separated from alcohol in needles melting at  $121-122^\circ$ :

0.2010 gave 0.6802  $CO_2$  and 0.1420  $H_2O$ .  $C = 92.28$ ;  $H = 7.84$ .

0.2005 „ 0.6785  $CO_2$  „ 0.1407  $H_2O$ .  $C = 92.28$ ;  $H = 7.79$ .

$C_{24}H_{24}$  requires  $C = 92.31$ ;  $H = 7.69$  per cent.

The straw-yellow oil, which was separated from the crystals, boiled at  $260-262^\circ$  (28 mm.):

0.1585 gave 0.536  $CO_2$  and 0.1135  $H_2O$ .  $C = 92.23$ ;  $H = 7.95$ .

$C_{24}H_{24}$  requires  $C = 92.31$ ;  $H = 7.69$  per cent.

Molecular weight determinations indicate that these substances are isomerides:

|  | Needles,<br>m. p. $121-122^\circ$ . | Oil, b. p. $260-262^\circ$<br>(28 mm.). |
|--|-------------------------------------|---|
| Weight of substance.....               | 0.3933                              | 0.2518                                  |
| „ solvent (chloroform) .....           | 22.52                               | 24.00                                   |
| Observed rise of the boiling point ... | $0.201^\circ$                       | $0.127^\circ$                           |
| Molecular weight .....                 | 318                                 | 302                                     |

Triphenylmethylecyclopentane,  $C_{24}H_{24} = 312$ .

In this case the yield of oil greatly exceeds that of the solid. The oil slowly changes into a crystalline form which is found to be identical with the needles (m. p. 121—122°).

*Reduction of Triphenylmethylocyclopentadiene.*

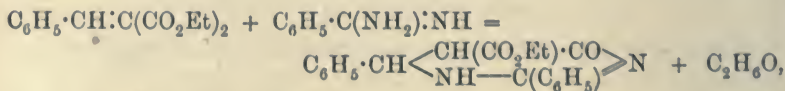
Four grams of the unsaturated hydrocarbon were reduced with a mixture of 2 grams of red phosphorus and 10 grams of hydriodic acid in a sealed tube at 200°. Very little oil was formed, but acicular crystals were obtained (m. p. 121°) which were identified as triphenylmethylocyclopentane.

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XLI.—*The Action of Ammonia and Organic Bases on Ethyl Esters of Olefinedicarboxylic and Olefine-β-Ketocarboxylic Acids.*

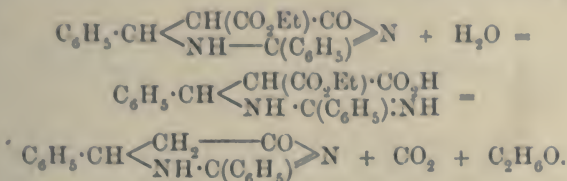
By SIEGFRIED RUHEMANN.

IN continuing my researches on the formation of heterocyclic compounds from unsaturated acids, I have examined the action of ammonia and benzamidine on the ethyl esters of olefinedicarboxylic acids and olefine-β-ketocarboxylic acids. Former investigators have already pointed out that these esters form additive products with great ease, and have described a number of such compounds obtained from the esters and organic bases; some of these derivatives are in turn readily transformed into cyclic compounds. I have found that benzamidine and ethyl benzyldienemalonate interact according to the following equation:

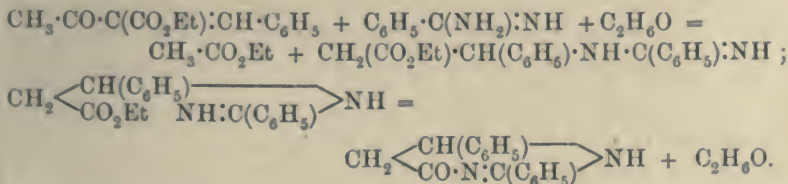


and yield *ethyl dihydrodiphenylpyrimidonecarboxylate*. This reaction is analogous to that which leads to the formation of diphenylpyrimidone from benzamidine and ethyl phenylpropiolate (Ruhemann and Stapleton, *Trans.*, 1900, 77, 239). Ethyl dihydrodiphenylpyrimidonecarboxylate, on treatment with ammonia, undergoes an interesting transformation: the ring opens, and then closes again with the loss

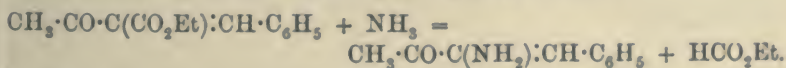
of carbon dioxide and alcohol, to yield *dihydrodiphenylpyrimidone*, thus :



Dihydrodiphenylpyrimidone is also obtained by the action of an alcoholic solution of benzamidine on ethyl benzylideneacetoacetate. Its formation takes place by the union of benzamidine with the unsaturated ester, accompanied by the removal of the acetyl group as ethyl acetate and the loss of alcohol, thus :



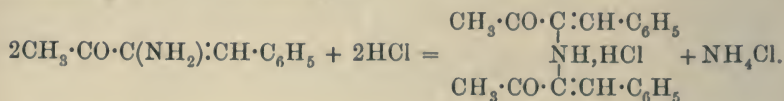
The interaction which occurs between ethyl benzylideneacetoacetate and benzamidine has induced me to examine also the action of this ester as well as that of different olefine- $\beta$ -ketocarboxylic esters on other bases. Up to the present, I have studied their behaviour towards ammonia. This study has led to the interesting fact that ethyl benzylideneacetoacetate reacts with ammonia in a manner different from the other olefine- $\beta$ -ketocarboxylic esters, which as yet have been subjected to this treatment. Ethyl ethylideneacetoacetate and ethyl furylideneacetoacetate are decomposed by ammonia into the aldehyde-ammonias and ethyl acetoacetate, which compounds subsequently condense to ethyl hydrocollidinedicarboxylate and ethyl hydrofuryllutidinedicarboxylate. Ethyl benzylideneacetoacetate, however, does not undergo an analogous condensation, but yields benzylidenaminoacetone, according to the following equation :



This reaction is somewhat similar to the decomposition which ethyl dicarboxylglutaconate suffers under the influence of ammonia and organic bases. Benzylidenaminoacetone is rather unstable, and readily loses benzaldehyde, especially on treatment with acids. Besides the aldehyde, another compound is formed, if benzylidenaminoacetone is warmed with concentrated hydrochloric acid. The ketone dissolves, and after a short time, the solution deposits a white,



crystalline solid, which is *diacetobenzylideneimide hydrochloride*. Its formation is to be expressed thus:



The hydrochloride is the intermediate product of the interaction between the acid and benzylideneaminoacetone, for on heating it with hydrochloric acid it decomposes, yielding benzaldehyde and another compound which is still under examination.

### EXPERIMENTAL.

#### *Ethyl Dihydrodiphenylpyrimidonecarboxylate.*

The action of benzamidine on ethyl benzylidenemalonate readily takes place by mixing solutions of sodium (1 at.) and the hydrochloride of the base (1 mol.) in alcohol, adding the ester (1 mol.), and heating the mixture on the water-bath. After a short time, the whole sets to a solid. This dissolves in boiling alcohol, and, on cooling, crystallises in colourless, silky needles which melt at 188°:

0.2095 gave 0.5425 CO<sub>2</sub> and 0.1080 H<sub>2</sub>O. C = 70.62; H = 5.72.

0.2983 „ 23 c.c. moist nitrogen at 20° and 758 mm. N = 8.79.

C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires C = 70.80; H = 5.59; N = 8.69 per cent.

Ethyl dihydrodiphenylpyrimidonecarboxylate dissolves in hydrochloric acid with the greatest ease, and therefore has the character of a base. At the same time, it has weak acidic properties, since the ester, although insoluble in cold caustic potash, gives a yellow coloration with sodium ethoxide when alcoholic solutions of both reagents are mixed. On evaporating off the alcohol, a yellow solid is left behind which is undoubtedly a sodium compound. This, however, turns white on adding water, and decomposes into the alkali and the unaltered ester. Ferric chloride produces a deep red coloration with an alcoholic solution of the ester.

#### *Action of Ammonia on Ethyl Dihydrodiphenylpyrimidonecarboxylate.*

The ester, when left in contact with concentrated aqueous ammonia, dissolves after about three weeks, yielding a yellow solution. This, when freed from ammonia as much as possible by warming on the water-bath under diminished pressure, gives, on neutralisation with hydrochloric acid, a white precipitate which dissolves in hot dilute

alcohol and crystallises from this solution in colourless needles melting at  $180^{\circ}$  :

0.2098 gave 0.5910  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ .  $\text{C} = 76.82$  ;  $\text{H} = 5.77$ .

0.5255 " 50.2 c.c. moist nitrogen at  $16^{\circ}$  and 764 mm.  $\text{N} = 11.20$ .

$\text{C}_{16}\text{H}_{14}\text{ON}_2$  requires  $\text{C} = 76.80$  ;  $\text{H} = 5.60$  ;  $\text{N} = 11.20$  per cent.

This compound, as stated above, is dihydrodiphenylpyrimidone. It is soluble with difficulty in cold alcohol, readily, however, on boiling, and the alcoholic solution gives a red coloration with ferric chloride. Dihydrodiphenylpyrimidone dissolves in dilute hydrochloric acid, as does also the monocarboxylic ester from which it is formed, but it differs from the latter inasmuch as it yields a platinichloride, whilst the ester does not.

The *platinichloride* is precipitated on adding platinic chloride to the solution of hydrodiphenylpyrimidone in hydrochloric acid. It forms small, orange prisms which are readily dissolved by hot water :

0.2725 gave 0.0580 Pt.  $\text{Pt} = 21.28$ .

$(\text{C}_{16}\text{H}_{14}\text{ON}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 21.37$  per cent.

#### *Action of Benamidine on Ethyl Benzylideneacetoacetate.*

This reaction takes place on mixing, in molecular proportions, sodium ethoxide and benamidine hydrochloride, dissolved in alcohol, then adding ethyl benzylideneacetoacetate (1 mol.), and digesting the mixture for about an hour. On distillation from the water-bath, ethyl acetate is removed together with the alcohol, and an oil is left behind which yields with water a semi-solid product. This dissolves in hot alcohol, and the solution, on cooling, deposits colourless prisms of dihydrodiphenylpyrimidone. The identity of this substance with the compound formed from the hydrodiphenylpyrimidonecarboxylic ester and ammonia is proved not only by the fact that the melting point and the other properties are the same, but also by the following analysis :

0.2102 gave 21 c.c. moist nitrogen at  $20^{\circ}$  and 742 mm.  $\text{N} = 11.15$ .

$\text{C}_{16}\text{H}_{14}\text{ON}_2$  requires  $\text{N} = 11.20$  per cent.

#### *Action of Ammonia on Ethyl Olefine- $\beta$ -ketocarboxylates.*

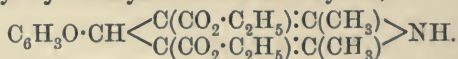
(i) Ethyl ethylideneacetoacetate,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{CO}_2\cdot\text{C}_2\text{H}_5):\text{CH}\cdot\text{CH}_3$ , when mixed with alcoholic ammonia, dissolves with a development of heat. The yellowish solution does not deposit any solid even after several days. On evaporation, a viscous product is left behind, which solidifies when treated with dilute hydrochloric acid. The substance crystallises from alcohol in colourless plates, which have a blue fluorescence and melt at  $131^{\circ}$ . These properties characterise it as ethyl

hydrocollidinedicarboxylate; its composition has, moreover, been verified by the following analysis:

0.2052 gave 0.4745  $\text{CO}_2$  and 0.1475  $\text{H}_2\text{O}$ .  $\text{C} = 63.06$ ;  $\text{H} = 7.98$   
 $\text{C}_{14}\text{H}_{21}\text{O}_4\text{N}$  requires  $\text{C} = 62.92$ ;  $\text{H} = 7.86$  per cent.

This reaction is to be explained by assuming that ethyl ethylideneacetoacetate first decomposes into acetaldehyde and the acetoacetic ester, which two compounds then condense with ammonia to form ethyl hydrocollidinedicarboxylate. This view is supported by the behaviour of ethyl ethylideneacetoacetate towards a solution of methylamine. On mixing the reagents, heat is developed, and acetaldehyde and ethyl acetoacetate are formed. On evaporating the yellow solution under diminished pressure on the water-bath and adding dilute hydrochloric acid to the small quantity of oily residue, a solid is obtained. This is ethyl hydrocollidinedicarboxylate, which owes its formation to the presence of traces of ammonia in the solution of methylamine which I have used.

(ii) Ethyl furylideneacetoacetate,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CO}_2 \cdot \text{C}_2\text{H}_5) : \text{CH} \cdot \text{C}_4\text{H}_8\text{O}$ , reacts with ammonia in a similar manner to the ethylideneacetoacetate, and yields ethyl hydrofuryllutidinedicarboxylate,



The ester is isolated from the ammoniacal solution, as in the former case, and recrystallised from alcohol. The melting point  $164^\circ$  agrees with Schiff and Puliti's statement (*Ber.*, 1883, 16, 1607):

0.2185 gave 0.5130  $\text{CO}_2$  and 0.1315  $\text{H}_2\text{O}$ .  $\text{C} = 64.03$ ;  $\text{H} = 6.69$ .

0.3047 „ 11.2 moist nitrogen at  $9^\circ$  and 765 mm.  $\text{N} = 4.53$ .

$\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}$  requires  $\text{C} = 63.95$ ;  $\text{H} = 6.58$ ;  $\text{N} = 4.39$  per cent.

(iii) Ethyl benzylideneacetoacetate,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CO}_2 \cdot \text{C}_2\text{H}_5) : \text{CH} \cdot \text{C}_6\text{H}_5$ , as stated in the introduction to this paper, behaves towards ammonia in a manner different from the other olefine- $\beta$ -ketocarboxylic esters, and yields a compound which is to be regarded as *benzylideneaminoacetone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{NH}_2) : \text{CH} \cdot \text{C}_6\text{H}_5$ .

This substance is formed by adding an excess of alcoholic ammonia to ethyl benzylideneacetoacetate; the ester dissolves, and the solution, when left overnight, sets to a semi-solid mass of colourless needles; these are insoluble in water, but readily dissolve in ether, chloroform, carbon bisulphide, or hot alcohol, but less soluble in cold alcohol.

Benzylideneaminoacetone may be crystallised by adding water to the warm alcoholic solution until it becomes cloudy; after a time, needles separate which melt at  $125^\circ$  to an oil which does not solidify on cooling. On boiling the alcoholic solution, decomposition takes place, which is indicated by the formation of benzaldehyde.



As benzylideneaminoacetone is not stable at 100°, it has been dried, for analysis, under diminished pressure at the ordinary temperature :

0.2175 gave 0.5915 CO<sub>2</sub> and 0.1357 H<sub>2</sub>O. C = 74.14 ; H = 6.91.  
 0.2085 „ 0.5685 CO<sub>2</sub> „ 0.1300 H<sub>2</sub>O. C = 74.36 ; H = 6.92.  
 0.2652 „ 20 c.c. moist nitrogen at 9° and 738 mm. N = 8.80.  
 0.2723 „ 19.7 c.c. „ 5° „ 751 mm. N = 8.74.  
 C<sub>10</sub>H<sub>11</sub>ON requires C = 74.53 ; H = 6.83 ; N = 8.69 per cent.

*Action of Hydrochloric Acid on Benzylideneaminoacetone.*

On heating with dilute hydrochloric acid, the ketone decomposes, and benzaldehyde separates out ; if, however, the ketone is carefully warmed with the concentrated acid, it dissolves, benzaldehyde is formed, and, at the same time, colourless crystals are deposited which are insoluble in alcohol or water, decompose at 210°, and melt at 215° to a brown liquid. The following analytical data indicate that the compound is the hydrochloride of diacetobenzylideneimide :

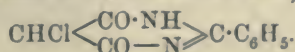
0.2600 gave 0.1075 AgCl. Cl = 10.23.  
 0.2678 „ 9.2 c.c. moist nitrogen at 18° and 770 mm. N = 4.02.  
 C<sub>20</sub>H<sub>19</sub>O<sub>2</sub>N.HCl requires Cl = 10.39 ; N = 4.10 per cent.

The filtrate from the imide, after removing the benzaldehyde by extraction with ether, yields on evaporation a solid which contains ammonium chloride, as has been proved by the preparation and the analysis of the platinichloride :

0.3760 left, on ignition, 0.1645 Pt. Pt = 43.75.  
 (NH<sub>3</sub>)<sub>2</sub>H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 43.84 per cent.

Diacetobenzylideneimide, on heating with dilute hydrochloric acid, decomposes ; the compound, however, which is formed along with benzaldehyde has not yet been carefully examined. I hope shortly to publish the result of this study, together with the outcome of the further researches on the behaviour of bases towards olefine-β-keto-carboxylic esters.

In conclusion, I may mention an experiment which has been undertaken with the view of condensing ethyl chloromalonate with benzamidine. It has been found, indeed, that a reaction takes place on mixing alcoholic solutions of sodium ethoxide with ethyl chloromalonate and heating the mixture on the water-bath, but that a replacement of the chlorine is not effected. The compound which is formed is the *benzamidide* of chloromalonic acid,



It is isolated from the product of the reaction by evaporating off

the alcohol, washing the dark residue with water, then dissolving this in ammonia, in which it is freely soluble, decolorising the solution with animal charcoal, and finally adding to the filtrate an excess of dilute hydrochloric acid. The white precipitate, which is thus formed, is insoluble in water or organic solvents, and does not melt at  $320^{\circ}$ :

0.2158 gave 0.4283  $\text{CO}_2$  and 0.0630  $\text{H}_2\text{O}$ .  $\text{C} = 54.12$ ;  $\text{H} = 3.24$ .

0.2252 „ 24.6 c.c. moist nitrogen at  $18^{\circ}$  and 765 mm.  $\text{N} = 12.70$ .

0.2332 „ 0.1493  $\text{AgCl}$ .  $\text{Cl} = 15.84$ .

$\text{C}_{10}\text{N}_7\text{O}_2\text{N}_2\text{Cl}$  requires  $\text{C} = 53.93$ ;  $\text{H} = 3.14$ ;  $\text{N} = 12.58$ ;  $\text{Cl} = 15.95$  per cent.

An analogous bromo-compound is formed on using ethyl bromomalonate.

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## XLII.—*Distillation of Chlorine Water.*

By ARTHUR RICHARDSON, Ph.D.

THE composition of chlorine water and its hydrate has from time to time occupied the attention of chemists ever since the discovery of hypochlorous acid by Ballard in 1833. Following on this discovery, we find the statement, "apparently due to Schönbein in the first instance, that the chlorine in chlorine hydrate is present as hypochlorous and hydrochloric acids, and that its composition is represented by the formula  $\text{HCl}, \text{HClO}, 9\text{H}_2\text{O}$ . It does not appear, however, that this statement was based on any direct experimental evidence, although indirectly it received some support from an observation of Millon made in 1849, who found that a mixture of the two acids was stable in very dilute solutions at the ordinary temperature. The abnormal solubility of chlorine in water observed by Roscoe (this Journal, 1856, 8, 15) at temperatures near that at which the hydrate is formed led him to suspect the formation of the oxy- and hydr-acids of chlorine in the solution. To determine whether they were present or not, he passed a stream of carbon dioxide through chlorine water, and led the escaping gas into a large volume of pure water, for since the oxy-acids are volatile it was to be expected that, if present, they would distil more or less completely from the first solution into the second, leaving excess of the less volatile hydrochloric acid behind. Analysis showed, however, that no such separation had taken place, but that the whole of the chlorine removed by the inert gas was present in the free state. Roscoe

therefore concluded that the oxy- and hydr-acids were absent from chlorine water. Copner (*Ber.*, 1875, 8, 287), commenting on the absence of confirmation for Schönbein's statement, assumed that the presence of hypochlorous and hydrochloric acids in chlorine hydrate was proved by the fact that mercuric chloride was formed on treating the hydrate with mercury (Waltner's reaction). Schiff (*Ber.*, 1875, 8, 419), on the other hand, showed that the same result was obtained when free chlorine was treated with the metal, this test failing to prove the presence of the two acids in the hydrate. Jakowkin (*Ber.*, 1897, 30, 515; *Zeit. physikal. Chem.*, 1899, 29, 613), from a study of the electrical conductivity of chlorine water, was led to the conclusion that very dilute solutions undergo dissociation into hydrochloric and hypochlorous acids,  $\text{Cl}_2\text{aq} \rightleftharpoons (\text{HCl} + \text{HClO})\text{aq}$ . He found the conductivity at  $0^\circ$  to be equal to that of hydrochloric acid containing the same amount of hydrogen chloride, and concluded that the oxy-acid is a non-electrolyte; the conductivity of the solution was much diminished with increased concentration. The recent photochemical researches of Mellor (*Trans.*, 1901, 79, 216; 1902, 81, 1280; Mellor and Anderson, *ibid.*, 1902, 81, 414; and Mellor and Russell, *ibid.*, 1902, 81, 1272), serve to emphasise the fact that chlorine gas, whether alone or in presence of hydrogen, is sensitive to light only when water is present; indeed, the new facts recorded and the exhaustive bibliography contained in these papers, whilst forming a valuable contribution to our knowledge of the subject, show also the need of further information regarding the composition of chlorine water, whether in the liquid or "gaseous" state, in order that the more complicated reactions brought about by light may be satisfactorily explained.

Closely connected with the present work is the observation, made many years ago by Pickering (*Trans.*, 1880, 37, 139), that when chlorine water was heated in an evaporating basin, an aqueous solution of hydrochloric acid remained after all the active chlorine had been expelled. This result, since confirmed by my own experiments, led me to inquire whether the formation of hydrochloric acid in the residue was accompanied by the separation of hypochlorous or other volatile oxy-acid, or whether the active chlorine escapes only in the free state. To test this, advantage was taken of the fact that when even very dilute aqueous solutions of hypochlorous acid are distilled, the oxy-acid, together with water, passes over below  $100^\circ$ . It seems probable, therefore, that by slowly distilling chlorine water, any oxy-acid present would be found together with free chlorine in the distillate.

*Separation of Free Chlorine from Hypochlorous Acid.*—Before approaching this problem, it was first necessary to devise some simple means of separating free chlorine from hypochlorous acid, since the



tests for the oxy-acid in the presence of free halogen are far from satisfactory. The difference between the vapour pressures of the two solutions affords a ready means of doing this: thus on passing an air current through chlorine water the free chlorine is rapidly removed, whilst a similar aspiration has but little effect on the strength of dilute solutions of the oxy-acid. This is seen to be the case from the following results obtained on estimating the active chlorine in samples of freshly prepared chlorine water, and of dilute solutions of hypochlorous acid, in each case before and after aspiration with a current of air saturated with moisture for 4 hours.

TABLE I.

| No. | Solution.   | Before aspiration.  | After aspiration.                                |
|-----|---|---|--|
| 1   | 100 c.c. chlorine water   | Active chlorine =<br>44 c.c. $N/10$ $Na_2S_2O_3$  | Active chlorine =<br>trace                       |
| 2   | 100 c.c. hypochlorous acid  | Active chlorine =<br>20 c.c. $N/10$ $Na_2S_2O_3$  | Active chlorine =<br>20 c.c. $N/10$ $Na_2S_2O_3$ |
| 3   | 100 c.c. hypochlorous acid  | Active chlorine =<br>92 c.c. $N/10$ $Na_2S_2O_3$  | Active chlorine =<br>90 c.c. $N/10$ $Na_2S_2O_3$ |
| 4   | <div> 50 c.c. chlorine water* }<br/> 50 c.c. hypochlorous acid } </div> | <div> Active chlorine =<br/>22 c.c. <math>N/10</math> <math>Na_2S_2O_3</math> }<br/> Active chlorine =<br/>45 c.c. <math>N/10</math> <math>Na_2S_2O_3</math> } </div> | Active chlorine =<br>44 c.c. $N/10$ $Na_2S_2O_3$ |

Such a process would obviously not apply to strong solutions where the vapour pressure of the acid is considerable; in the present work, however, we are concerned only with solutions of the same order of strength as those just indicated. This method was therefore applied to the separation of free chlorine from the products of distillation of chlorine water in the experiments now to be described.

Chlorine water was first prepared with chlorine generated by the action of hydrochloric acid on potassium dichromate, the gas being passed through water, then through a solution of chromic acid contained in a tube 1 metre long placed in an oblique position, and finally through water in a washing bulb, the exit tube of which was sealed to a delivery tube dipping into the water to be saturated with the gas.

\* Here it is seen that the free chlorine in chlorine water is completely removed by aspiration, whereas the strength of solutions of hypochlorous acid is only little altered by the process, whilst in a mixture of the free halogen and oxy-acid the former only is withdrawn by the air.

*Distillation of Chlorine Water.*

*Experiment I.*—When 500 c.c. of water, saturated with chlorine at the ordinary temperature and pressure, were gently heated in a retort, drops of distillate soon began to pass over together with free chlorine. In 2 hours, 48 c.c. were collected, although the contents of the retort had at no time been allowed to boil. After the lamp was removed, an additional 10 c.c. of liquor distilled over from the hot solution. In the first place, the excess of free chlorine was removed from the 58 c.c. of distillate collected by aspiration with a current of air. After 2 hours, the smell of chlorine had entirely disappeared, but the solution was still rich in active chlorine, for it liberated iodine freely from potassium iodide, immediately bleached indigo solution, and on shaking with mercury gave a brownish-yellow deposit resembling that obtained with hypochlorous acid, and in this respect differing entirely from the slaty-grey precipitate formed when ordinary chlorine water was treated with the metal.

The residual solution in the retort still smelt of free chlorine, and 100 c.c. were subjected to aspiration. After 2 hours, the solution failed to liberate a trace of iodine from potassium iodide, and reddened but did not bleach litmus; it gave a white precipitate of silver chloride with silver nitrate, thus proving the presence of hydrochloric acid.

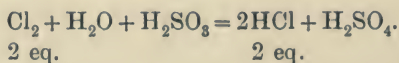
In this experiment, the preparation and distillation of chlorine water was conducted in the diffused light of an Indian summer day; it seemed possible, therefore, that the results here obtained might be due to photo-chemical action, since Peddler (*Trans.*, 1890, 57, 613) has shown that the oxy-acids of chlorine are formed by the action of diffused light on chlorine water.

*Experiment II.*—Fresh chlorine water was therefore prepared and distilled in a dark room. In this, as in the former experiment, the distillate, after removal of free chlorine, bleached indigo, freely liberated iodine from potassium iodide, and gave the characteristic yellow precipitate with mercury. The residual solution contained hydrochloric acid, this result proving that the changes observed in the first experiment are not due to the action of light; to avoid complications, however, all the subsequent experiments were made in a dark room.

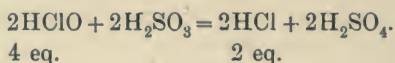
*Experiment III.*—The last experiment was next repeated with washed chlorine, further purified by conversion into the hydrate at  $0^{\circ}$ , the gas evolved from the melting crystals having been led into redistilled water. Distillation of the chlorine water so prepared gave a distillate similar in all respects to that obtained in the previous experiments; the residual solution contained hydrochloric acid, thus showing that further purification of the chlorine does not

influence the result obtained. From these qualitative experiments it is seen that, when chlorine water is heated, a mixture of free chlorine and an oxy-acid passes off, leaving hydrochloric acid in the solution.

In order to study this reaction, it was first necessary to further characterise the oxy-acid. For this purpose, the total chlorine and also the active form of this element were estimated in the distillate after removing the free chlorine by aspiration. Now it is obvious that a comparison of the values so obtained will serve as an indication of the condition of the active chlorine present; thus, if it is in the free state, the values found by the iodometric method will agree with those obtained for the total chlorine estimated as silver chloride after treatment with sulphurous acid:



If, on the other hand, the halogen is present as an oxy-acid, this agreement will no longer hold; thus in the case of hypochlorous acid the active chlorine will be represented by a value double that found for the total chlorine:



*Analytical Method.*—The active chlorine was estimated iodometrically with *N*/10 sodium thiosulphate after addition of potassium iodide and hydrochloric acid. The volumetric estimation of the total chlorine is, however, complicated by the excess of sulphurous acid, added in the first instance, which is precipitated as silver sulphite in neutral solutions. Roscoe (*loc. cit.*) overcame this difficulty by estimating the chloride gravimetrically in the solution acidified with nitric acid. The large number of estimations demanded by the present work, however, called for some simple means of removing the excess of sulphur dioxide in order that the chloride might be estimated volumetrically. In order to do this, the original solution containing excess of sulphurous acid was largely diluted, and then heated in an evaporating basin at a temperature just below the boiling point; by this means, the sulphur dioxide was rapidly expelled, so that on adding potassium chromate no trace of green chromic chloride was formed; the cold solution was then neutralised with sodium hydrogen carbonate and the titration with silver nitrate carried out in the usual way.

The accuracy of the method, on which the later results entirely depend, is seen on comparing the values obtained for the active and total chlorine found in dilute chlorine water, as estimated by *N*/10 thiosulphate and silver nitrate respectively, as follows:



TABLE II.

| Sample. | Active chlorine.  | Total chlorine.  |
|---------|---|--|
| No. 1 { | 10 c.c. = 3.65 c.c. $N/10$ $Na_2S_2O_3$<br>20 c.c. = 7.20 " " | 10 c.c. = 3.7 c.c. $N/10$ $AgNO_3$<br>20 c.c. = 7.25 " " |
| No. 2 { | 10 c.c. = 4.60 " "<br>20 c.c. = 9.25 " "                      | 10 c.c. = 4.60 " "<br>20 c.c. = 9.30 " "                 |
| No. 3 { | 10 c.c. = 11.60 " "<br>10 c.c. = 11.50 " "                    | 10 c.c. = 11.5 " "<br>" " " "                            |

Having decided these preliminary points, the active and total chlorine in the products of distillation of chlorine water were therefore estimated in this way.

*Analytical Results.*—Freshly prepared chlorine water (1000 c.c.), when distilled for 6 hours at a temperature just below the boiling point, yielded 77 c.c. of distillate. After 2 hours' aspiration, the active and total chlorine in one portion of the distillate was estimated with the following result, calculated for the total distillate: active chlorine = 26.1 c.c.  $N/10$   $Na_2S_2O_3$ ; total chlorine = 14 c.c.  $N/10$   $AgNO_3$ .

Here the proportion of active to total chlorine found is not far removed from the ratio 2:1. The remainder of the distillate was again aspirated for 4 hours to remove any free chlorine still present. Analysis then gave: active chlorine = 22.3 c.c.  $N/10$   $Na_2S_2O_3$ ; total chlorine = 11.0 c.c.  $N/10$   $AgNO_3$ .

The active chlorine is here represented by a value almost exactly double that found for the total chlorine, showing that it is present as hypochlorous acid.

Analysis of the residual solution in the retort, after aspiration for 2 hours in the cold, gave for the total residue: active chlorine, absent; total chlorine = 29.3 c.c.  $N/10$   $AgNO_3$ .

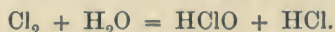
This value, which is seen to be largely in excess of the total chlorine found in the distillate, shows that under the conditions of the experiment the reacting chloride is not equally divided between the two acids. It seemed probable, however, that this result might be due to the gradual decomposition of part of the hypochlorous acid, under the prolonged action of heat, which was inevitable during distillation for 6 hours at temperatures below the boiling point; the process was therefore modified to overcome this difficulty.

Chlorine water was now distilled at the boiling point in a stream of

chlorine gas, the solution being heated in a distilling flask, through which a stream of chlorine was passed by means of an inlet tube ground into the neck of the flask, and sealed to the water bulb connected with the washing apparatus of the chlorine generators. The side tube was sealed to the inner tube of a Liebig's condenser, the distillate being collected in the small open distilling flask from which excess of free chlorine was removed by means of a side tube attached to an aspirator. After 400 c.c. of chlorine water had been rapidly distilled in a current of the gas until 195 c.c. of distillate had passed over, the free chlorine was removed from the distillate and residue by aspiration for 4 hours, and the two solutions were analysed:

| Total distillate (195 c.c.).   | Total residue (205 c.c.)                          |
|--|---|
| Active chlorine = 48.7 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$ | Active chlorine absent.                           |
| Total       ,,       = 25.9       ,, $\text{AgNO}_3$                 | Total chlorine = 25.6 c.c. $N/10$ $\text{AgNO}_3$ |

This experiment indicates that at the boiling point, as at lower temperatures, hypochlorous acid passes over when chlorine water is distilled, and that the values obtained for the total chlorine in the distillate and residue are now in close agreement, showing that the reacting chlorine is equally divided between the two acids. Under these conditions, therefore, the change is represented by the equation:



Even under these more favourable conditions, the proportion of hydrochloric acid tends to increase with slow distillation and prolonged digestion. Thus, in one case, in which 50 c.c. only were allowed to distil over in 8 hours, the total chlorine in the residue reached a value double that found in the distillate.

This led me to test the stability of chlorine water at the boiling point when distillation and the consequent separation of the two acids were altogether prevented, the object being to determine whether hydrochloric acid was a decomposition product of the action of heat on chlorine water, or whether it was strictly a dissociation product depending for its separation on the isolation of hypochlorous acid in the distillate. To decide this, a fresh quantity of chlorine water was heated in the same apparatus as before, but in this case the flask was fitted with an upright condenser so that the distillate returned to the distilling flask. A continuous stream of chlorine was passed through 400 c.c. of the solution, which was kept at the boiling point for 5 hours, the free chlorine being then removed in the cold. Analysis gave for the total volume: active chlorine absent; total chlorine = 4 c.c.  $N/10$   $\text{AgNO}_3$ .

In a second experiment, when the solution was boiled for 3 hours, it contained, after aspiration, no active chlorine, and total chlorine = 1.7 c.c.  $N/10$   $\text{AgNO}_3$ .

The small amount of chloride found under these conditions shows that, when the separation of the two acids is prevented, chlorine water undergoes very little decomposition at the boiling point. These results also indicate that the formation of the two acids during distillation is due to the removal of one of the acids from the sphere of action, and not to the action of the chlorine water on the alkali contained in the glass. We are therefore led to the conclusion that hypochlorous and hydrochloric acids are separated during distillation as the products of the partial change of chlorine water.

This conclusion is further justified by the fact that, on mixing the residue and distillate obtained by distilling chlorine water, a solution having all the properties of the original chlorine water is reproduced. Thus, in one experiment, 160 c.c. of distillate were collected from 400 c.c. of chlorine water distilled in a current of chlorine gas; the free chlorine was then removed from the residue and distillate by aspiration until the air-current, when passed through a solution of potassium iodide, failed to liberate a trace of iodine. The two solutions were then analysed:

| Total distillate.  | Total residue.                                    |
|--|---|
| Active chlorine = 52 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$ . | Active chlorine absent.                           |
| Total chlorine = 26.5 c.c. $N/10$ $\text{AgNO}_3$ .                  | Total chlorine = 28 c.c. $N/10$ $\text{AgNO}_3$ . |

Half of the residue and a similar proportion of the distillate were then mixed, with the result that the product now smelt of free chlorine, and on renewed aspiration, the escaping air freely liberated iodine from potassium iodide.

Analysis of the aspirated solution now gave: active chlorine absent, total chlorine = 3 c.c.  $N/10$   $\text{AgNO}_3$ , thus showing that mutual decomposition of the two acids with evolution of free chlorine had taken place.



The conditions which influence the change were now further studied. In the first place, an experiment was made to determine whether the two acids are actually formed by the action of chlorine on water at the boiling point, or whether they have their origin in the cold solution, distillation in such a case serving only to separate the acids first formed. To decide this, 400 c.c. of pure water were first heated to the boiling point and then saturated with chlorine gas, the distillation being carried out as before; 100 c.c. of distillate contained, after aspiration: active chlorine = 40 c.c.  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ ; total chlorine = 21 c.c.  $N/10$   $\text{AgNO}_3$ .



The residue contained no active chlorine, and total chlorine = 36.5 c.c.  $N/10$   $\text{AgNO}_3$ .

These results show that at the boiling point chlorine reacts with water, forming the oxy- and hydr-acids. The composition of the distillate before and after removal of the free chlorine by aspiration was now determined, in order to gain some idea as to the proportion of hypochlorous acid to free chlorine passing over in solution in the distillate. To do this, the last experiment was repeated, 160 c.c. of distillate being collected from the distillation of 400 c.c. of solution. Analysis gave for the total distillate :

|  |   |       |   |   |      |   |   |                   |  |
|--|---|-------|---|---|------|---|---|-------------------|--|
| Before aspiration, active chlorine = 162.0 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$ . |   |       |   |   |      |   |   |                   |  |
| After  | „ | „     | „ | = | 42.4 | „ | „ | „                 |  |
| „  | „ | total | „ | = | 20.9 | „ | „ | $\text{AgNO}_3$ . |  |

Here it is seen that about one-quarter of the active chlorine in the original distillate is present as hypochlorous acid.

In very dilute solutions, the whole of the free chlorine taken appears to enter into reaction with the water. Thus, in a series of experiments in which solutions of chlorine water of different degrees of dilution were distilled from a retort, the values for the active and total chlorine found in the distillates without previous aspiration approached more nearly to the ratio 2 : 1 as dilution increased ; finally, chlorine water containing active chlorine (= 20 c.c. of  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ ) in 2000 c.c. of water were distilled ; 90 c.c. of distillate gave, without previous aspiration, active chlorine = 3.6 c.c.  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ , total chlorine = 1.8 c.c.  $N/10$   $\text{AgNO}_3$ , showing that, in this case, all the free chlorine taken had reacted with the water, hypochlorous acid alone passing over into the distillate.

The next experiment was made to determine the amount of hypochlorous acid formed at the different stages of the distillation. Three fractions (each of 80 c.c.) were collected from 400 c.c., of pure water distilled in a stream of chlorine gas, the rate of the gas current and of the distillation being kept as nearly uniform as possible. Analysis after removal of free chlorine gave the values tabulated on p. 389.

These numbers show that the yield of hypochlorous acid steadily diminishes as distillation proceeds ; though in each fraction the close agreement between the values found for the active and total chlorine with those required by theory for hypochlorous acid is well maintained. This decrease in yield is such as might be expected, since the removal of the oxy-acid in the distillate is attended by the separation of fresh hydrochloric acid in the residual solution, reaching in this case a value = 54.2 c.c.  $N/10$   $\text{AgNO}_3$  when the last fraction had passed over ; the concentration of the acid already formed also tends to increase as the water distils off in the process.

| Fraction.                        | Active chlorine.                                   | Total chlorine.                  |
|----------------------------------|--|----------------------------------|
| Distillate (1). 80 c.c. ....     | 40.2 c.c. $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$ | 20.6 c.c. $N/10$ $\text{AgNO}_3$ |
| " (2). 80 " ....                 | 23.4 " "   | 11.6 " "                         |
| " (3). 80 " ....                 | 16.1 " "   | 8.7 " "                          |
| Total distillate = 240 c.c. .... | 79.7 " "   | 40.9 " "                         |
| Residue = 160 c.c. ....          | Absent   | 54.2 " "                         |

The influence of hydrochloric acid on the dissociation was further studied in the following experiment, in which the solutions described below were distilled in a stream of chlorine; 60 c.c. of distillate in each case were collected, the active chlorine, as hypochlorous acid, being estimated after the removal of free chlorine by aspiration.

(1) 150 c.c. of pure water gave active chlorine in the distillate = 28.8 c.c.  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ .

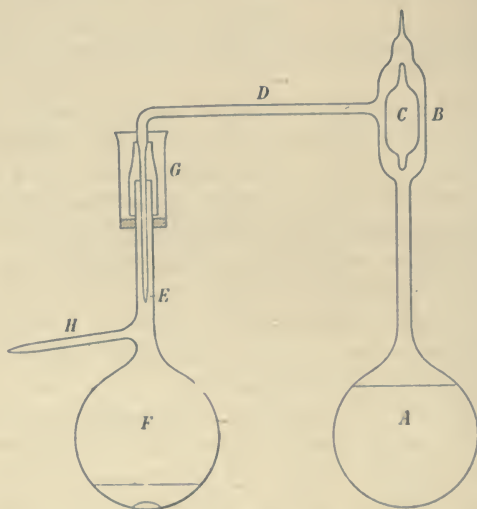
(2) 150 c.c. of water containing  $\text{HCl}$  = 25.9 c.c.  $N/10$   $\text{AgNO}_3$  gave a distillate containing active chlorine = 12 c.c.  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ .

(3) 150 c.c. of the residual solution from a previous experiment, in which  $\text{HCl}$  = 25.9 c.c.  $N/10$   $\text{AgNO}_3$  had already been formed during distillation, was again distilled; the distillate contained active chlorine = 13 c.c.  $N/10$   $\text{Na}_2\text{S}_2\text{O}_3$ . Thus the presence of hydrochloric acid, whether added to or formed in the solution, causes a marked decrease in the yield of hypochlorous acid passing over during distillation.

The results of a large number of experiments made to determine the strength of hydrochloric acid required to arrest entirely the formation of the oxy-acid during distillation—that is, to ensure complete stability of the chlorine water—showed that it was not until a strength equal to 1 part of concentrated  $\text{HCl}$  to 8 parts of chlorine water had been reached that the oxy-acid ceased to distil over.

In conclusion, an experiment was made to investigate the dissociation of chlorine water at the ordinary temperature; this was done by distilling the solution under diminished pressure in the apparatus indicated (p. 390). This consisted of a bolt-head flask, *A*, the neck of which was enlarged at *B* and contained a tube *C* of 15 c.c. capacity, previously filled with dry chlorine and sealed, the end of *B* being also drawn out and sealed. Water (500 c.c.) was boiled in *A* until all the air had been expelled by the side tube, *D*, which was then sealed up at its drawn-out extremity. When the water in *A* was cold, the bulb *C* was broken inside *B* and the flask shaken until the chlorine was absorbed. By means of the india-rubber tube

and mercury cup *G*, the end of *E* was tightly fixed in the neck of the flask *F*, which was provided with a side tube, *H*, and contained 50 c.c. of water and a globule of mercury. The water in *F* was now boiled to expel all the air, and *H* was sealed off. The two flasks were then connected by breaking the capillary *E* inside the neck of *F*, and, on placing *F* in a freezing mixture, the liquid in *A* distilled into *F*. The distillate, when finally shaken with the mercury, gave rise to the brownish-yellow precipitate characteristic of



hypochlorous acid, showing that the oxy-acid passes over from chlorine water under diminished pressure at the ordinary temperature.

From these experiments it is shown :—

- (1) That when chlorine water is distilled, it undergoes partial change with formation of hypochlorous and hydrochloric acids,
- (2) That when the separation of the two acids is prevented, chlorine water is practically stable at the boiling point,
- (3) That the amount of change decreases as distillation proceeds, owing to the formation of hydrochloric acid in the original solution, and that in the presence of a large excess of the acid only free chlorine passes over in the distillate.



### XLIII.—*A Series of Double Chromates.*

By SAMUEL HENRY CLIFFORD BRIGGS.

WHILST recently engaged in investigating the existence of the normal chromates of copper, nickel, and the allied metals, I was led to examine the action of potassium and ammonium chromates on various metallic salts in concentrated aqueous solution. In this way, the salt,  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , was prepared, as well as an isomorphous mixture  $\text{K}_2\text{Ni}[\text{SO}_4, \text{CrO}_4]_2 \cdot 6\text{H}_2\text{O}$ .

A double salt,  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ , resulted when a concentrated ammonia solution was added to the solution of the compound  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and the copper, cadmium, and zinc double salts crystallising with two molecules of ammonia have also been obtained.

As these results have no direct bearing on the original object of the research, which is not yet completed, it was decided to publish them separately.

#### *The Isomorphous Mixture, $\text{K}_2\text{Ni}[\text{CrO}_4, \text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ .*

Although very small quantities of potassium chromate gave basic salts with nickel chloride or nitrate, equivalents of nickel sulphate and potassium chromate could be mixed in solution without immediate precipitation.

Ten grams of potassium chromate in 17 c.c. of water were added to 14.6 grams  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  in 20 c.c. water, the solutions having been previously cooled in ice. The crystals which separated were collected and dried as quickly as possible with filter paper, and then in a desiccator.

On analysis, a specimen was found to contain 17.72 per cent.  $\text{CrO}_3$ . This result corresponds with an isomorphous mixture,  $\text{K}_2\text{Ni}[\text{CrO}_4, \text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ , which requires 17.15 per cent.  $\text{NiO}$  and 21.14 per cent.  $\text{SO}_3$ , whereas the amounts actually found were 17.34 per cent.  $\text{NiO}$ , and 21.40 per cent.  $\text{SO}_3$ .

The only double salt of potassium chromate of this class which has yet been obtained is the compound  $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The double sulphate corresponding to this crystallises with  $6\text{H}_2\text{O}$ . It is therefore of interest to find that the nickel compounds both crystallise with six molecules of water. All attempts to prepare the double salt,  $\text{K}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in a pure state have as yet proved unsuccessful.

*Nickel Ammonium Chromate,  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ .*

This compound, which was first obtained by the action of ammonium chromate on nickel silicofluoride in concentrated water solution, is more conveniently prepared by the use of the chloride, nitrate or acetate, the last of these being the best, as in this case the preparations are not complicated by the separation of basic salts.

Twenty-four grams of ammonium chromate dissolved in 50 c.c. of water were added in the cold to 20 grams of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 20 c.c. of water. The double salt, which crystallised out on standing, was collected and separated from basic salt by dissolving a few grams at a time in a small quantity of water at  $40^\circ$ , and allowing the solution to crystallise. The mother liquor was poured off, filtered, and used for the next portion, the crystals being washed with a little water and dried in the air:

| Analyses.            | Found.          | Required for<br>$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ . |
|----------------------|-----------------|--|
| $\text{CrO}_3$ ..... | 45.89 per cent. | 46.01 per cent.  |
| $\text{NiO}$ .....   | 17.30 „         | 17.22 „  |
| $\text{NH}_3$ .....  | 7.94 „          | 7.83 „   |

Since this double chromate, unlike its constituents, could be recrystallised from water, whereas nickel chromate has never been obtained from aqueous solution, and ammonium chromate can only be recrystallised from water containing a large excess of ammonia, it appeared probable that the solution of the double salt would contain complex ions, complete dissociation not having taken place. This view was supported by freezing point determinations:

|        |                |   |
|--------|----------------|---|
| 0.2032 | in 9.941 water | gave $\Delta t$ $0.370^\circ$ , $M = 104.0$ . |
| 0.4221 | „ 9.941        | „ $0.645^\circ$ , $M = 124.0$ .               |
| 0.6539 | „ 13.146       | „ $0.730^\circ$ , $M = 128.5$ .               |

Since  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2$  has a molecular weight of 328, complete dissociation into five ions would give a molecular weight in solution of 65.6. The experiments could not be extended over a wider range of concentrations, since the 5 per cent. solution is saturated at the freezing point, whilst solutions containing less than 2 per cent. of the double chromate deposit a basic salt very readily, and consequently do not give satisfactory values for the depression of the freezing point.

The decomposition of the double salt in solution is very much affected by the addition of other substances, alcohol or cane sugar for example causing a copious precipitation of basic salts.

Locke (*Amer. Chem. J.*, 1902, 27, 280) has recently drawn attention to the many points of difference between the chromates and sulphates,

particularly with reference to the formation of double salts. Attempts have therefore been made to obtain double chromates by the action of ammonium chromate on salts of cadmium, zinc, manganese, and copper, but so far these have proved unsuccessful; amorphous precipitates being the usual result. Equivalents of ammonium chromate and cadmium or zinc silicofluoride could be mixed in suitably concentrated solutions without precipitation, but the liquids had the orange colour of the  $\text{Cr}_2\text{O}_7^-$  anion, and evidently contained basic salts in solution, which were deposited on cooling in ice, and dissolved again on heating or on dilution.

*The Double Chromates,  $(\text{NH}_4)_2\text{M}^{\text{II}}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ .*

This series of double chromates probably corresponds in constitution with the crystalline salts containing two molecules of water, such as  $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2\text{Ca}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  (*Zeit. physikal. Chem.*, 1902, 42, 1—16). That the compounds are derivatives of chromic acid and not dichromic acid is evident from their formation in alkaline solution and also from the lemon-yellow colour of the zinc salt.

Although insoluble in cold water, these salts are decomposed by hot water, and are readily dissolved by dilute acids or ammonia solution. They undergo no change when heated for several hours at  $100^\circ$ , but ammonia is given off below  $200^\circ$ , and a sudden decomposition occurs between  $200^\circ$  and  $300^\circ$ , giving rise to a mixture of oxides.

*Nickel Salt,  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ .*—In the preparation of  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$  from nickel chloride, a sample of ammonium chromate had been used, which contained dichromate. After removal of the double salt, ammonia solution was added to the mother liquor with the intention of converting the dichromate into chromate, and then obtaining a better yield. Brownish-red crystals separated instead of the bright green hexahydrate. The red crystals were washed with water, dried in the air, and analysed, and found to have the composition required by the formula  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ :

|                        | Found.          | Required.       |
|------------------------|-----------------|-----------------|
| NiO.....               | 20.83 per cent. | 20.71 per cent. |
| CrO <sub>3</sub> ..... | 55.38 " "       | 55.42 " "       |
| NH <sub>3</sub> .....  | 18.76 " "       | 18.87 " "       |

Preparations were also made by the following methods:

(1) An excess of ammonia was added to an aqueous solution of  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; the liquid slowly evolved ammonia and yielded a brown precipitate which was apparently a basic salt. This was dissolved in ammonia, and although the solution was allowed to



remain in the air once more, no crystals were formed. The addition of another ammonium salt, such as the chloride or nitrate, however, caused the crystallisation of the compound required, the separation of which was very much aided by scratching the walls of the containing vessel.

(2) Twelve grams of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in 25 c.c. of water and 18 grams of  $(\text{NH}_4)_2\text{CrO}_4$  in 40 c.c. of water were added. Concentrated ammonia solution in excess was then added and the mixture allowed to remain in the air, when the brown crystals of the double salt separated out. After thorough washing with water and dilute ammonia, these crystals contained no sulphate. Hence, it must be concluded that a double sulphate crystallising with two molecules of ammonia isomorphous with the double chromate is not produced under the conditions of the experiment.

When the compound  $(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$  was heated it evolved water and ammonia below  $200^\circ$ , and underwent sudden decomposition at  $280\text{--}290^\circ$ , giving a black, shining powder. The residue was 64.4 per cent. of the original substance, and was probably a mixture of  $\text{Ni}_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$  which corresponds with 64.8 per cent. residue, whereas  $\text{NiO} \cdot \text{Cr}_2\text{O}_3$  requires 62.9.

*Copper Salt*,  $(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ .—Ten grams of copper carbonate and 26 grams of chromium trioxide were dissolved in a little water and the solution made up to 200 c.c. Concentrated ammonia solution was added until a clear liquid was obtained, which after filtering was allowed to remain in the air. The double chromate separated in large, black, shining crystals, these were filtered off, washed with dilute ammonia and dried in the air; the yield was 25 grams. When seen in thin layers by transmitted light, the crystals were yellow, but in larger quantities they were deep green:

|                      | Found. | Required for<br>$(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ . |
|----------------------|--------|---|
| $\text{CuO}$ .....   | 21.70  | 21.67   |
| $\text{CrO}_3$ ..... | 54.54  | 54.77   |
| $\text{NH}_3$ .....  | 18.82  | 18.64   |

When heated, the compound began to give off water and ammonia below  $200^\circ$ , and decomposed suddenly with incandescence between  $240^\circ$  and  $250^\circ$ , leaving a voluminous residue of the mixed oxides  $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ .

*Zinc Salt*,  $(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ .—In the first attempt to prepare this compound 10 grams of zinc hydroxide and 20 grams of chromium trioxide were used, the preparation being carried out in exactly the same way as described for the copper compound. As the excess of ammonia was given off the solution did not crystallise but became coated with a gelatinous scum, which dissolved when ammonia

was added but was deposited again on standing. The addition of another ammonium salt such as the chloride or nitrate prevented this, and caused the required compound to separate in bright, lemon-yellow crystals. When an excess of chromium trioxide was used, for example, 26 grams to 10 grams of the hydroxide, the double salt separated without the addition of another ammonium salt. It therefore seems probable that the excess of ammonium chromate formed in the last instance had the same effect as the ammonium chloride in the first experiment, the action being, perhaps, due to the increase in concentration of ammonium ions thus produced :

|                      | Found. | Required for<br>$(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2, 2\text{NH}_3$ . |
|----------------------|--------|--|
| $\text{CrO}_3$ ..... | 54.41  | 54.44  |
| $\text{NH}_3$ .....  | 18.44  | 18.53  |

When the substance was heated it blackened below  $200^\circ$  giving off water and ammonia, and decomposed suddenly at  $255$ — $270^\circ$ , leaving a voluminous residue, which amounted to 64.9 per cent. of the compound heated.  $\text{ZnO}, \text{Cr}_2\text{O}_3$  requires 63 per cent.

*Cadmium Salt*,  $(\text{NH}_4)_2\text{Cd}(\text{CrO}_4)_2, 2\text{NH}_3$ .—The preparation was made from 26 grams of chromium trioxide and 13 grams of cadmium oxide in the same way as with the copper and zinc compounds. After a day or two, large, yellow crystals separated from solution ; these were analysed with the following result :

|                      | Found. | Required for<br>$(\text{NH}_4)_2\text{Cd}(\text{CrO}_4)_2, 2\text{NH}_3$ . |
|----------------------|--------|--|
| $\text{CdO}$ .....   | 31.23  | 30.84  |
| $\text{CrO}_3$ ..... | 48.36  | 48.58  |
| $\text{NH}_3$ .....  | 16.32  | 16.45  |

The crystals when heated became darker in colour, and underwent sudden decomposition at  $280$ — $290^\circ$ , giving a residue with a bright grey, metallic lustre, probably a combination of the oxides. A residue of 67.62 per cent. was left on heating the salt, whereas  $\text{CdO}, \text{Cr}_2\text{O}_3$  requires 67.61.

THE YORKSHIRE COLLEGE,  
LEEDS.

XLIV.—*The Chlorine Derivatives of Pyridine. Part VIII. The Interaction of 2:3:4:5-Tetrachloropyridine with Ethyl Sodiomalonate.*

By W. J. SELL, M.A., F.R.S., and F. W. DOOTSON, M.A., D.Sc.

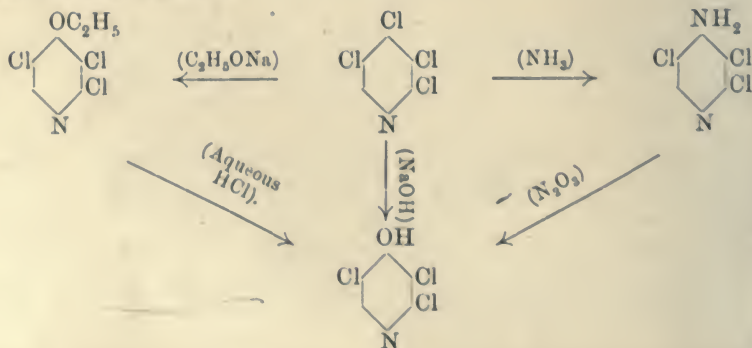
THE interesting syntheses which have been effected by the action of the sodium compounds of ethyl malonate on various halogen derivatives by Conrad, Bischoff, and others, and more especially by W. H. Perkin, jun., suggested that this reagent might be of use in the syntheses of carboxy and other derivatives of pyridine. Previous experience has shown that the more highly chlorinated pyridines, although they exhibit a high degree of stability towards most of the ordinary reagents, are nevertheless attacked by alkalis at moderate temperatures, with the displacement of at least one chlorine atom.

The first compound experimented on in this direction was 2:3:4:5-tetrachloropyridine, and a preliminary trial having been attended with success, a considerable quantity of material was worked up in the manner indicated, a good yield being obtained of a compound in which one chlorine atom of the tetrachloropyridine was replaced by the group  $-\text{CH}(\text{CO}_2\text{Et})_2$ .

The particular chlorine atom displaced is regarded as the one which occupies the para-position relatively to the nitrogen atom, and in support of this hypothesis the following facts may be cited.

Ammonia interacts with 2:3:4:5-tetrachloropyridine, giving 2:3:5-trichloro-4-aminopyridine (Trans., 1900, 77, 3). The latter substance was converted into the corresponding hydroxy-derivative by the action of nitrosulphonic acid and shown to be identical with the compound obtained by the interaction of 2:3:4:5-tetrachloropyridine with alcoholic or aqueous sodium hydroxide.

Sodium ethoxide reacts with 2:3:4:5-tetrachloropyridine, yielding an oil which, on prolonged boiling with aqueous hydrochloric acid, gives rise to 2:3:5-trichloro-4-hydroxypyridine. These relationships may be thus indicated:

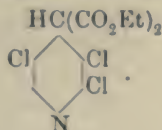




In none of these cases under the conditions tried was there any evidence that a chlorine atom other than the one occupying the para-position relatively to nitrogen was removed.

Moreover, since in 2:3:4:5-tetrachloropyridine the remaining hydrogen atom is adjacent to nitrogen, it is *prima facie* improbable that the chlorine atom in position 2 would be easily replaceable, and thus far it has not been found possible to replace the chlorine atoms in positions 3 or 5 in any of the chloropyridines.

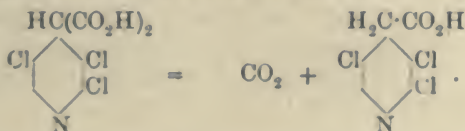
The above facts leave little room for doubting that ethyl trichloropyridylmalonate is correctly represented by the following formula :



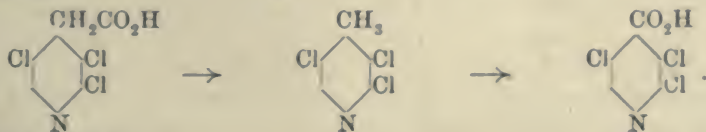
Although many methods of hydrolysis were tried both in acid and alkaline solutions, a loss of carbon dioxide always accompanied the process, and all attempts to isolate the dicarboxylic acid were unsuccessful. On the other hand, by the interaction of moderately concentrated sulphuric acid, a good yield of the monocarboxy-derivative, trichloropyridylacetic acid, was obtained, the change involved being thus represented :



The dicarboxylic acid then breaks down in the following way :



The monocarboxylic acid thus obtained is non-volatile ; it melts at 144—145°, losing carbon dioxide and being converted quantitatively into 2:3:5-trichloro-4-methylpyridine, which latter, on boiling with alkaline permanganate solution, is slowly oxidised to trichloroisonicotinic acid. The relationship of these substances may be represented as follows :



An attempt to obtain sufficient trichloropyridine for identification from the silver salt of trichloroisonicotinic acid was unsuccessful owing to the small amount of acid available, but it is hoped to repeat this part of the work.

#### EXPERIMENTAL.

*Conversion of 2:3:4:5-Tetrachloropyridine into Ethyl Trichloropyridylmalonate.*—Preliminary trials having shown that ethyl sodiummalonate reacts on heating with 2:3:4:5-tetrachloropyridine, replacing one chlorine atom, and that longer boiling than 10 hours is prejudicial, the plan finally adopted for the preparation of ethyl trichloropyridylmalonate was as follows. Ethyl malonate (96 grams) was added to a solution of 13·8 grams of sodium in 300 c.c. of absolute alcohol, followed, after thorough agitation, by 60 grams of the tetrachloropyridine. These quantities represent rather more than 2 molecules of ethyl sodiummalonate to 1 of the tetrachloropyridine. The whole was then boiled in a reflux apparatus for about 10 hours, the alcohol being then distilled off and the liquid acidified with dilute sulphuric acid. The separated oil was then washed repeatedly with water, dried *in vacuo*, and fractionated under a pressure of about 28 mm. until a temperature of 150° was reached, when the operation was stopped. The distillate contained a small quantity of the unchanged tetrachloropyridine, but consisted mainly of ethyl malonate, more than half of the quantity employed being thus recovered. In view of this result, experiments were tried with a diminished proportion of ethyl sodiummalonate, when the yield was found to be perceptibly diminished.

After some hours, the dark-coloured residual liquid remaining in the flask became solid, or nearly so. This was moistened with alcohol, drained at the pump, and washed with small quantities of the solvent, until a crop of almost colourless crystals remained. On purification from alcohol, these separated in colourless, massive forms which melted sharply at 63–64° (uncorr.):

0·1624 gave 0·2488 CO<sub>2</sub> and 0·0489 H<sub>2</sub>O. C = 41·77; H = 3·34.

0·3947 „ 0·4943 AgCl. Cl = 30·94.

0·3217 „ 10·9 c.c. nitrogen at 17° and 770 mm. N = 3·99.

C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>NCl<sub>3</sub> requires C = 42·29; H = 3·52; Cl = 31·27; N = 4·11 per cent.

The ethyl trichloropyridylmalonate, as thus prepared, is readily soluble in alcohol, ether, and the usual organic solvents, and insoluble in water. It dissolves in dilute solutions of the caustic alkalis, and is reprecipitated on acidifying. If to its solution in aqueous caustic potash a strong solution of this reagent be added, a potassium salt separates in colourless crystals which may be recrystallised from a hot,

moderately strong solution of the alkali. A potassium determination gave the following numbers :

0.2290 gave 0.0520  $K_2SO_4$ .  $K = 10.18$ .

$C_{13}H_{11}O_4NCl_3K$  requires  $K = 10.30$  per cent.

*Conversion of Ethyl Trichloropyridylmalonate into Trichloropyridylacetic Acid.*—All attempts made to hydrolyse ethyl trichloropyridylmalonate so as to obtain the corresponding acid were unsuccessful. Prolonged boiling, either with alcoholic solutions of caustic alkalis or with dilute acids, was ineffective, and treatment with a carbon disulphide solution of aluminium chloride left the substance unaltered. Trichloropyridylacetic acid was formed on dissolving the compound in sulphuric acid containing approximately 80 per cent. of the acid and heating for some time on the water-bath, or more rapidly by boiling for a few minutes. The cold solution was poured into water and the filtered precipitate recrystallised from boiling water, which, on cooling, deposited a crop of colourless crystals in the form of rectangular plates melting at  $144-145^\circ$  (uncorr.):

0.3622 gave 0.4578  $CO_2$  and 0.0535  $H_2O$ .  $C = 34.47$ ;  $H = 1.64$ .

0.3214 „ 0.4040  $CO_2$  „ 0.0475  $H_2O$ .  $C = 34.28$ ;  $H = 1.64$ .

0.3370 „ 0.6077  $AgCl$ .  $Cl = 44.77$ .

0.4513 „ 22.5 c.c. nitrogen at  $18^\circ$  and 760 mm.  $N = 5.75$ .

$C_7H_4O_2NCl_3$  requires  $C = 34.92$ ;  $H = 1.66$ ;  $N = 5.82$ ;  $Cl = 44.24$  per cent.

Trichloropyridylacetic acid readily dissolves in the usual organic solvents and in boiling water, but is sparingly soluble in cold water. If to a solution in hot water, silver nitrate is added, a white, granular precipitate separates on cooling. This silver salt is sparingly soluble in boiling water, from which it crystallises on cooling in rosettes of needles. The calcium salt is soluble. The barium salt, in the presence of ammonia, slowly separates in long needles.

*Conversion of Trichloropyridylacetic Acid into 2:3:5-Trichloro-4-methylpyridine.*—Trichloropyridylacetic acid, as mentioned above, is non-volatile, and on heating at  $144^\circ$  melts with decomposition, carbon dioxide being freely evolved. If the pressure be reduced to 20—25 mm. and the temperature raised to about  $160^\circ$ , trichloropicoline distils over, the yield being nearly quantitative.

As obtained in this manner, the substance is practically pure; it crystallised from alcohol in long, colourless needles which melt sharply at  $31-31.5^\circ$  (uncorr.):

0.3186 gave 0.4230  $CO_2$  and 0.0618  $H_2O$ .  $C = 36.21$ ;  $H = 2.15$ .

0.1057 „ 0.2310  $AgCl$ .  $Cl = 54.16$ .

$C_6H_4NCl_3$  requires  $C = 36.61$ ;  $H = 2.03$ ;  $Cl = 54.28$  per cent.



This substance exhibits the same general solubility as the chloropyridines, which it closely resembles in appearance and odour. It is volatile at the ordinary temperature, and rapidly disappears when left exposed to the air.

*Conversion of 2:3:5-Trichloro-4-methylpyridine into 2:3:5-Trichloropyridine-4-carboxylic Acid.*—The trichloropicoline described above was boiled for some hours with a slight excess of potassium permanganate, in a flask provided with a reflux apparatus. The excess of permanganate was removed by alcohol, and, after filtering off the separated hydrated manganese dioxide, the colourless filtrate was evaporated to a small bulk and acidified with dilute sulphuric acid. When allowed to remain in a desiccator, large, colourless crystals separated which melted constantly at  $188\text{--}189^\circ$  (uncorr.), and from which the following numbers were obtained:

0.1632 gave 0.1890  $\text{CO}_2$  and 0.0316  $\text{H}_2\text{O}$ .  $\text{C} = 31.60$ ;  $\text{H} = 0.91$ .

$\text{C}_6\text{H}_2\text{O}_2\text{NCl}_3$  requires  $\text{C} = 31.78$ ;  $\text{H} = 0.88$  per cent.

The acid is very soluble in hot water, and the ordinary organic solvents, but only sparingly so in cold water.

*Conversion of 2:3:4:5-Tetrachloropyridine into 2:3:5-Trichloro-4-hydroxypyridine.*

(a) By sodium ethoxide.

When 2:3:4:5-tetrachloropyridine was added to a hot solution of sodium ethoxide in absolute alcohol, a separation of sodium chloride immediately took place with considerable evolution of heat. The mixture, after heating on the water-bath for half an hour, was diluted with water and acidified, when an oil separated.

The hydroxide, obtained by boiling this oily ethoxide for half an hour with concentrated hydrochloric acid, separated in fine, colourless needles, which, on purification from alcohol or boiling water, melted sharply at  $216\text{--}217^\circ$  (uncorr.), and were identical in properties with the 2:3:5-trichloro-4-hydroxypyridine described below:

0.1288 gave 0.2780  $\text{AgCl}$ .  $\text{Cl} = 53.56$ .

0.1420 „ 9.8 c.c. nitrogen at  $19^\circ$  and 748 mm.  $\text{N} = 7.20$ .

$\text{C}_5\text{H}_2\text{ONCl}_3$  requires  $\text{Cl} = 53.65$ ;  $\text{N} = 7.05$  per cent.

(b) By aqueous or alcoholic caustic soda.

The interaction of 2:3:4:5-tetrachloropyridine with boiling dilute caustic soda solution (1:10) is slow; but if the process is continued in a reflux apparatus until all the oily drops have disappeared, 2:3:5-trichloro-4-hydroxypyridine, melting at  $216\text{--}217^\circ$  (uncorr.), is obtained in theoretical yield on acidifying the product with dilute sulphuric acid;

0.0970 required 14.7 c.c.  $N/10$   $\text{AgNO}_3$ .  $\text{Cl} = 53.8$ .

$\text{C}_5\text{H}_2\text{ONCl}_3$  requires  $\text{Cl} = 53.65$  per cent.

If to the aqueous caustic soda sufficient alcohol be added to completely dissolve the oil, or if alcoholic soda be used, the reaction proceeds smoothly and rapidly, the same product being obtained on acidifying, as is attested by its melting point and general properties.

*Conversion of 2:3:5-Trichloro-4-aminopyridine into 2:3:5-Trichloro-4-hydroxypyridine.*

The trichloroaminopyridine obtained by the action of ammonia on 2:3:4:5-tetrachloropyridine, the constitution of which has been previously determined (*loc. cit.*), was dissolved in sulphuric acid and an excess of nitrosulphonic acid added. After warming the mixture on the water-bath for half an hour, the whole was poured into water, and the crystalline precipitate purified by solution in caustic soda solution, reprecipitation by acid, and subsequent crystallisation from hot water or dilute alcohol. The substance thus obtained melted at  $216-217^\circ$  (uncorr.):

0.5270 gave 32.0 c.c. nitrogen at  $15^\circ$  and 752 mm.  $\text{N} = 7.04$ .

$\text{C}_5\text{H}_2\text{ONCl}_3$  requires  $\text{N} = 7.05$  per cent.

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## XLV.—On Colour Changes observed in Some Cobalt Salts.

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

IN an interesting communication by Dr. Donnan and Mr. Bassett (Trans., 1902, 81, 939), there is a reference to work of mine on the action of heat on the absorption spectra and chemical constitution of saline solutions (*Sc. Trans. Roy. Dub. Soc.*, 1900, 7, [ii], 253; Abstr., 1901, ii, 53). I quote the authors' words: "It is evident from the spectra that solutions of cobalt chloride in hydrochloric acid and in saturated calcium chloride solutions contain something which is also produced in the strong aqueous solution on rise of temperature. This is regarded by Hartley as the anhydrous chloride, and adduced as evidence in support of the hydration theory, but the facts admit of another interpretation, as will be shown in the course of this paper."

There are two inaccuracies here, both of which are rather misleading,

and as the paper, although only recently published, was for the most part written twenty-three years ago, it has been carefully examined in order to ascertain if the authors had perhaps been led by any inadvertent statement of mine to misinterpret both the facts and the conclusions deduced therefrom. I do not find this to be the case.

In the first place, it is by no means evident that solutions of cobalt chloride in hydrochloric acid contain something which is produced in strong aqueous solutions on rise of temperature, because the absorption spectrum, which is not affected by heat, is different from those shown at any temperature between  $20^{\circ}$  and  $100^{\circ}$  by pure aqueous solutions, and the difference is such as to lead to the conclusion that the acid solution contains something which is different. Secondly, the colour of hot solutions of cobalt chloride was not attributed to the anhydrous salt, but to the presence of the dihydrate in solution. Lastly, these spectra were not photographed, but observed with the eye, and drawn to scale from measurements by a method fully described. To photograph such spectra would have been impossible.

*The Spectra of Various Solutions of Cobalt Chloride.*—The six spectra observed in a solution of cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , saturated at  $20^{\circ}$ , and heated to  $23^{\circ}$ ,  $33^{\circ}$ ,  $43^{\circ}$ ,  $53^{\circ}$ ,  $73^{\circ}$ , and  $93^{\circ}$ , are none of them identical either with the spectrum of anhydrous chloride dissolved in alcohol, or with that of cobalt chloride in hydrochloric acid, in fact, they exhibit several important differences (*loc. cit.*, Plate XX, Figs. *A*, *B*, and *C*).

For instance, they exhibit broad absorption curves, as well as narrow, straight bands which extend beyond *F* to *G*, whilst the hydrochloric acid solution is chiefly characterised by a broad band between *D* and *F*, without curvature, but having a nearly perpendicular boundary.

The absorption increases in intensity with increased thickness of the layer of liquid, but the absorption as observed by me did not extend to regions of either greater or lesser wave-length. With the band at the red end it is different, the greater the thickness of the layer of liquid the further the absorption extends towards rays of shorter wave-length, that is to say, from near *C* to between *D* and *E*.

The extension of the absorption is approximately proportional to the thickness of the layer of absorbing medium, as may be seen by the angle which the edge of the band makes with the perpendicular, this being about the angle of the prism of liquid contained in the wedge-shaped cells. It is probable that this colour is due to a compound of cobalt chloride with hydrochloric acid, for the following reason. When anhydrous cobalt chloride is suspended in anhydrous ether, in which it is quite insoluble, a blue soluble substance is formed on passing dry hydrogen chloride into the liquid. A part of the chloride, when not anhydrous, appears also as a blue liquid not dissolved



by the ether, in which it is but sparingly soluble. By analogy also with cupric chloride, it is possible that such a compound may be produced, since Engel has shown that cupric chloride combines with hydrochloric acid, and the formula of one salt of this type has been given as  $\text{CuCl}_2 \cdot 3\text{H}_2\text{O} \cdot \text{HCl}$ .

Similarly, the spectrum of cobalt chloride in alcohol does not exactly resemble that of any of the other solutions. This is easily accounted for by alcohol combining with the chloride to form a crystallisable alcoholate. Such a compound was obtained and analysed by F. Bourion (*Compt. rend.*, 1902, 134, 472), to which the formula  $2\text{CoCl}_2 \cdot 5\text{C}_2\text{H}_5 \cdot \text{OH}$  was assigned. This proves what was inferred from the spectrum of the solution in alcohol—namely, that the colour was due to a blue alcoholate.

Regarding the solutions in alcohol, it will be seen on p. 300 of the original memoir that "The blue solution in alcohol was proved not to be an alcoholate." Although it was believed that an alcoholate was formed, various endeavours to obtain and isolate it had proved futile, most probably because the experiments had been made with more or less hydrated cobalt chloride instead of with the anhydrous salt. Mr. J. A. Cunningham, working with me in 1900, obtained blue crystallised alcoholates which were easily decomposed by heat.

The aqueous saturated solution of cobalt chloride, when heated at  $93^\circ$ , contained something which also differed from that in alcohol or in hydrochloric acid. When the salt,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , was dissolved in 98 per cent. alcohol (*loc. cit.*, experiment recorded on pp. 299—300), the observations made pointed to the conclusion that the hexahydrate was converted into the dihydrate, but the hexahydrate crystallised out from the alcohol unchanged when the solution was evaporated without rise of temperature. I have given in detail special reasons for believing that the action of heat on an aqueous solution saturated at  $20^\circ$ , when warmed to  $100^\circ$ , likewise forms the dihydrate, and not the anhydrous salt.

In similar circumstances, the dihydrates are formed from the hexahydrated cobalt bromide and iodide. Now the black cobalt iodide dissolves in alcohol with an indigo-blue colour, but the brown hexahydrate yields an alcoholic solution having a rich green colour (*loc. cit.*, tabulated statement and notes, pp. 302—304), which is identical with the green colour of the solid  $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$ , and with the solution of the hexahydrate in water when heated above  $50^\circ$  and up to  $100^\circ$ .

Hence we arrive at the conclusion that the dihydrate is in solution, and not the anhydrous salt. It was also shown that the gradual change in the colour of the iodide on rise of temperature justifies the inference that at temperatures intermediate between  $20^\circ$  and  $53^\circ$  there are variable mixtures of  $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$ .

*Double Salts of Cobalt Chloride with Zinc Chloride and with Mercuric Chloride.*—There are some other points in the paper by Dr. Donnan and Mr. Bassett—namely, the action of zinc chloride or mercuric chloride on cobalt chloride solution, and also the action of heat on solid cobalt sulphate—which call for some comment. Von Babo explained the action of zinc chloride, when added to the solution of cobalt chloride, in preventing the solution from turning blue when the temperature is raised by assuming the formation of a double salt of the two chlorides, which on heating, as I have suggested, never attains to the condition of a dihydrate (*loc. cit.*, p. 266).

That the solution of mercuric chloride when added to cobalt chloride causes the formation of a complex molecule in an alcoholic solution, as observed by Donnan and Bassett, is easily accounted for by the formation of Claudet's salt, the double cobalt-mercuric chloride. It was from this finely crystallised compound that the preparations of pure cobalt salts were originally made for the purpose of spectroscopic examination.

*Cobalt Sulphate under the Action of Heat.*—The observations on p. 278 are apparently not in perfect agreement with those of Dr. Donnan and Mr. Bassett. They say, "It is known that the red anhydrous cobalt sulphate becomes violet when heated." The pure anhydrous cobalt sulphate, according to my recorded experiments, has a rose-pink colour; it may be heated at 300° with scarcely any perceptible change. If the heating be carried to 500° and beyond, approaching even to a red heat, it assumes a lilac colour, redder and less blue than lavender, and much paler than violet. It regains its original rose colour on cooling.

The salt is just on the point of decomposition when it attains its lilac tint, and if the heating be continued cobalt oxide is formed. If there is any trace of nitrate or chloride, or ammonium salt in the crystallised cobalt sulphate, it becomes purple as it melts, even violet or blue if the proportion of impurity is at all considerable. On heating a finely crystallised specimen of the double ammonium cobaltous sulphate in a platinum basin with oil of vitriol, a purple solution was at first produced. On raising the temperature until sulphur trioxide was freely evolved, much of the cobalt sulphate became insoluble and of the same lilac colour as the hot dry solid substance; on removing the source of heat, it quickly regained its rose-pink colour. After an interval of about 12 hours, the sulphuric acid was again heated until a vigorous decomposition of the sulphuric acid occurred, but there was no change of colour, the anhydrous salt remained rose-pink. The experiment was repeated under slightly different conditions, by heating the pure anhydrous sulphate in oil of vitriol contained in glass vessels. There was practically no difference between the hot and the cold solutions when viewed by transmitted light. The darkening of anhydrous

salts and oxides by the action of heat without evidence of chemical change is a well-known property, examined and described by Ackroyd, and termed metachromism.

*Cobalt Nitrate under the Action of Heat.*—The anhydrous nitrate becomes dark purple, but only just at the moment of its decomposition. This has been explained as being probably due to the formation of an oxynitrate.

Donnan and Bassett explain the production of a blue solution during the electrolysis of cobalt chloride by the formation at the anode of a complex ion having possibly the composition  $\text{CoCl}_4$  or  $\text{Co}_2\text{Cl}_3$ , and this may be correct, since Faraday has shown that when fused stannous chloride is electrolysed, stannic chloride passes to the anode and tin to the cathode.

There is a marked tendency for cobaltous salts to become converted into cobaltic compounds which are rather unstable, but if this action actually occurs, there should be little difficulty in separating and analysing the solutions containing these complex ions so as to determine the ratio of cobalt to chlorine in the manner indicated by Steele and Denison (*Trans.*, 1902, 81, 456). It may be remarked that to compare mere similarities in colour is a less precise method of examination than that of observing absorption spectra through varying thicknesses of solution and can give but little evidence of chemical constitution unless the changes of colour are very marked and are practically identical with those of substances already known and capable of identification by their colour. Such cases are so few as to be exceptional. The colour changes are, however, broadly marked in cobalt halogen salts, and we know the differences which occur when differently hydrated salts are crystallised. As a rule, the larger the number of water molecules the further removed is the colour of the crystals from that of the anhydrous salt and the more nearly does it approach the colour of water.

The views expressed in my paper—namely, that hydrated salts can exist in highly concentrated solutions, and can undergo dissociation owing to rise of temperature—account precisely for the facts observed, and apply to a number of concomitant phenomena; but the changes associated with cobalt chloride are less remarkable than those observed with many other salts, and they are comparatively of little importance.

The electrolysis of cobalt solutions has been investigated by Coehn and Glaser (*Zeit. anorg. Chem.*, 1902, 33, 9–24; *Abstr.*, 1903, 84, ii, 80), who showed that a deposit of oxide, always more or less hydrated, takes place on the anode—thin layers had the composition  $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , whilst the thicker layers corresponded with  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . These would account for a blue colour in the solution, when chlorine, hydrochloric acid, or cobaltous chloride was also present.

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XLVI.—*The Molecular Rearrangement of N-substituted Iminoethers*

By G. D. LANDER.

THE transformation of the atomic grouping  $-C(OR):N-$  into  $-CO\cdot NR-$  is a well-known phenomenon, which has been observed and studied chiefly by Gabriel and Neumann, Knorr, Wheeler and pupils, Hofmann, W. Wislicenus and Goldschmidt, and Wislicenus and Körber. References to the work of these chemists are given in the sequel.

The rearrangement in question has been found to occur most easily under the catalytic influence of alkyl iodides, but also appears to take place by simple heating.

The present paper contains a description of the results of experiments on the isomeric change of some of the recently prepared *N*-substituted open-chain iminoethers, and is divided into two sections, dealing with the catalytic rearrangement, which does not seem to have been studied for these substances, and the rearrangement by simple heating.

Apart from an extension of the data bearing on this topic, the object of the present work was mainly to determine whether the general conditions affecting the rearrangement would throw light on the difference in behaviour of most acylarylamines, on ethylation and methylation by means of dry silver oxide, for whereas the former process leads to the formation of iminoethers, the latter, under like conditions, brings about the simultaneous production of iminoethers and isomeric substituted amides (Trans., 1901, 79, 690).

I. *The Catalytic Rearrangement of N-substituted Iminoethers.*

The value of alkyl iodides in inducing isomeric change was first shown by Knorr (*Ber.*, 1897, 30, 929), who examined the isomeric change of the *O*-ethyl ethers of carbostyryl and  $\gamma$ -lepidone into *N*-methyl compounds by means of methyl iodide.

The rearrangement of many of the  $:NH$  iminoethers by similar means has been examined by Wheeler and pupils (*Amer. Chem. J.*, 1900, 23, 136).

Of the *N*-substituted iminoethers recently described (Trans., 1901, 79, 690; 1902, 81, 591; and this vol., 1903, 83, 320), the catalytic change has been studied with most of the *N*-arylacetimino-, *N*-arylbenzimino-, and *N*-alkyl-, and *N*-benzylbenzimino-ethers, with results which afford a general confirmation, and extension, of formerly recorded observations. A summary of the cases examined, and results obtained, is given in the following table:

| Iminoether.                                     | Catalyser.                                    | Temperature and period of heating. | Product of rearrangement.                     | Approximate extent of rearrangement. |
|---|---|------------------------------------|---|--------------------------------------|
| <i>N-Arylacetiminoethers:</i>                   |   |                                    |   |                                      |
| MeC(OMe):NPh                                    | MeI (0.5 mol.)                                | 100°: 15 hours                     | MeCO·NMePh                                    | Complete                             |
| MeC(OEt):NPh                                    | EtI (0.5 " )                                  | 100: 15 "                          | MeCO·NEtPh                                    | Very slight                          |
| MeC(OEt):NPh                                    | MeI (0.5 " )                                  | 150: 8 "                           | MeCO·NEtPh                                    | Complete                             |
| MeC(OEt):NPh                                    | MeI (1 " )                                    | 150: 8 "                           | MeCO·NMePh                                    | Complete                             |
| MeC(OEt):N·C <sub>6</sub> H <sub>4</sub> Me (o) | EtI (0.5 " )                                  | 150: 8 "                           | MeCO·NEt·C <sub>6</sub> H <sub>4</sub> Me (o) | About one-half                       |
| MeC(OEt):N·C <sub>6</sub> H <sub>4</sub> Me (p) | EtI (0.5 " )                                  | 150: 8 "                           | MeCO·NEt·C <sub>6</sub> H <sub>4</sub> Me (p) | Complete                             |
| <i>N-Arylbenziminoethers:</i>                   |   |                                    |   |                                      |
| PhC(OMe):NPh                                    | MeI (0.5 mol.)                                | 100°: 15 hours                     | PhCO·NMePh                                    | About three-fourths                  |
| PhC(OEt):NPh                                    | EtI (0.5 " )                                  | 150—160°: 13 "                     | PhCO·NEtPh                                    | Almost complete                      |
| PhC(OEt):NPh                                    | { EtCl (trace in }<br>{ alcoholic solution) } | 150—160°: 13 "                     | PhCO·NEtPh                                    | Nil                                  |
| PhC(OEt):NPh                                    | EtBr (0.5 mol.)                               | 200: 6 "                           | PhCO·NEtPh                                    | Slight                               |
| PhC(OMe):N·C <sub>6</sub> H <sub>4</sub> Me (o) | MeI (0.5 " )                                  | 130: 8 "                           | PhCO·NMe·C <sub>6</sub> H <sub>4</sub> Me (o) | Complete                             |
| PhC(OEt):N·C <sub>6</sub> H <sub>4</sub> Me (o) | EtI (0.5 " )                                  | 160: 13 "                          | PhCO·NEt·C <sub>6</sub> H <sub>4</sub> Me (o) | Nearly complete                      |
| PhC(OMe):N·C <sub>6</sub> H <sub>4</sub> Me (p) | MeI (0.5 " )                                  | 100: 15 "                          | PhCO·NMe·C <sub>6</sub> H <sub>4</sub> Me (p) | Complete                             |
| PhC(OEt):N·C <sub>6</sub> H <sub>4</sub> Me (p) | EtI (0.5 " )                                  | 160: 13 "                          | PhCO·NEt·C <sub>6</sub> H <sub>4</sub> Me (p) | Nearly complete                      |
| <i>N-Alkylbenziminoethers:</i>                  |   |                                    |   |                                      |
| PhC(OMe):NMe                                    | MeI (trace)                                   | 100°: 8 hours                      | PhCO·NMe <sub>2</sub>                         | Complete                             |
| PhC(OEt):NMe                                    | EtI ( " )                                     | 160: 6 "                           | PhCO·NMeEt                                    | Complete                             |
| PhC(OMe):NEt                                    | MeI ( " )                                     | 160: 2 "                           | PhCO·NMeEt                                    | Complete                             |
| PhC(OEt):NEt                                    | EtI ( " )                                     | 160: 6 "                           | PhCO·NEt <sub>2</sub>                         | Complete                             |
| <i>N-Benzylbenziminoethers:</i>                 |   |                                    |   |                                      |
| PhC(OMe):N·CH <sub>2</sub> Ph                   | MeI (trace)                                   | 100°: 12 hours                     | PhCO·NMe·CH <sub>2</sub> Ph                   | Complete                             |
| PhC(OEt):N·CH <sub>2</sub> Ph                   | EtI ( " )                                     | 120—130: 8 "                       | PhCO·NEt·CH <sub>2</sub> Ph                   | Incomplete                           |

*Experimental and Analytical Details of Experiments summarised in Table.*

In all cases, the iminoethers were heated in sealed tubes, and in order to minimise the formation of iodine, the halides (following Wheeler and Johnson) were introduced in sealed bulbs, which were broken after the tube had been closed. The identity of the products of transformation was established by melting point determinations in the case of solids, and in the case of liquids by analysis, details of which are omitted in the case of substances already described.

In the experiments on the *N*-arylacetiminoethers, the presence of unaltered imino-compound could be detected by distillation under the ordinary pressure (Trans., 1901, 79, 691); with the *N*-substituted benzimino-compounds, small quantities of iminoether were detected by the formation of benzoic esters on distillation with dilute hydrochloric acid in a current of steam, the same process sufficing for the isolation of small quantities of benzoylated secondary amines, which remained as oils, after complete distillation of the esters. An experiment with *N*-*p*-tolylbenziminomethyl ether showed that, after prolonged heating with dilute acid in a current of steam, the distilling flask contained nothing but a solution of *p*-toluidine hydrochloride with a little benz-*p*-tolylamide, formed by the action of the acid on the iminoether, and this result also proved that a benzoylated secondary amine was not present in the original substance.

Some of the benzoylated secondary amines have not yet been described.

*Benz-o-tolylmethylanide*, after recrystallisation from ether and light petroleum, forms prisms melting at 65—66°. C=80.05; H=6.8;  $C_{15}H_{15}ON$  requires C=80.0; H=6.66 per cent.

The isomeric *benz-p-tolylmethylanide* crystallises in prisms from ether and light petroleum melting at 46—48°. C=79.9; H=6.70.

*Benz-o-tolylethylanide* crystallises from ether and light petroleum in prisms melting at 71—72°. C=80.4; H=7.2;  $C_{16}H_{17}ON$  requires C=80.3; H=7.1; N=5.85 per cent.

The isomeric *benzethyl-p-tolylanide* crystallises in prisms from ether and light petroleum, melting at 38—40°. N=6.0 per cent.

*Benzbenzylmethylanide* is a viscid liquid boiling between 213° and 214° under 11 mm. pressure. N=6.3;  $C_{15}H_{15}ON$  requires N=6.2 per cent.

*Benzbenzylethylanide* is a liquid boiling at 214—216° (12 mm.). Found N=5.9; calculated N=5.85 per cent.



*Discussion of the Catalytic Rearrangement of Iminoethers.*

As mentioned in the introduction, the result of the experiments described is a general confirmation of those previously obtained. The importance of certain structural conditions, as determining the relative ease of rearrangement, is, however, more fully revealed.

It is, for example, clearly shown that, amongst the iminoethers, the methyl is distinctly more labile than the ethyl group; in no case does the transformation of an ethyl iminoether occur to a marked extent at 100°, whereas the corresponding methyl compounds, as a rule, undergo rearrangement quantitatively at that temperature. In the mixed products obtained by treating silver cyanurate at 100° with the appropriate iodides, the proportion of *O*-methyl to *N*-methyl ester is less than that of *O*-ethyl to *N*-ethyl ester, and Ponomareff (*Ber.*, 1885, 18, 3271) explained this difference by assuming that methyl isocyanurate is transformed more easily than the ethyl compound, a suggestion which is borne out by the results described in this communication.

The displacement of a higher by a lower alkyl, when an iminoether is heated with a lower alkyl iodide as in the following example,  $\text{CH}_3\text{C}(\text{OEt})\text{:NPh} + \text{MeI} = \text{CH}_3\text{CO}\cdot\text{NMePh} + \text{EtI}$ , was first noticed by Knorr, and subsequently by Wheeler and Johnson, and is a comparable phenomenon. It seemed of interest to examine the transformation of an iminoether by a higher alkyl iodide, and *N*-phenylbenziminomethyl ether and *n*-propyl iodide were selected. Molecular proportions of these substances were treated together for 4 hours at 150–160°, and finally, for 2 hours, at 200°. On distillation in a vacuum, an oily liquid, free from iminoether, was obtained which deposited crystals when sown with benzphenylmethylamide. The greater part of this oil was hydrolysed, and the secondary base acetylated, when, on distilling, a solid was obtained which began to fuse at 40°, melted completely at 76°, or at 80–97° after drying on a porous tile. This substance was evidently a mixture of acetphenylmethylamide and acetphenyl-*n*-propylamide, *n*-propyl iodide thus causing the conversion of the iminoether into both methyl- and *n*-propyl-amides. Although an accurate estimate of the relative proportions could not be made, it appears that the methyl compound preponderates in the mixture, and the experiment demonstrates the superior catalysing power of methyl iodide, for, in the first instance, only a small proportion of that compound would be formed— $\text{PhC}(\text{OMe})\text{:NPh} + \text{Pr}^n\text{I} = \text{PhCO}\cdot\text{NPr}^n\text{Ph} + \text{MeI}$ —and this small amount proves more efficacious in inducing isomeric change than the relatively large proportion of the higher iodide which is also present.

Of the three ethyl halides, the chloride scarcely induces isomeric

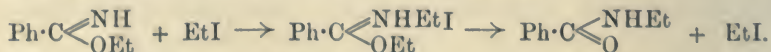
change, whilst the bromide does so to a considerably less extent than the iodide.

The ease of rearrangement depends also on the constitution of the iminoether, the *N*-arylbenziminooethers requiring either longer heating or a higher temperature than the iminoethers of lower molecular weight. Orientation of the aryl group exercises an influence, as will be seen from a comparison of the transformations of *N*-*o*-tolyl with *N*-phenyl and *N*-*p*-tolyl compounds, the former class undergoing isomeric change with greater difficulty than the latter. This accords with the previously recorded differences in the methylation of the corresponding acylated amines by means of dry silver oxide and methyl iodide, and also with the relative stability of certain *N*-*o*-tolyliminoethers.

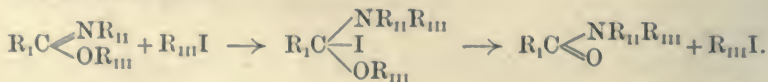
The rearrangement of the *N*-aryliminoethers takes place quite easily, but secondary reactions seem to occur with the *N*-alkyl and *N*-benzyl compounds. It is preferable to use a mere trace of iodide, as when a moderate quantity is employed, a distinct odour of an amine is noticeable on opening the tube, and small amounts of colourless solids are produced, which contain iodine and have a high melting point. These have not been identified with certainty, but are probably substituted ammonium iodides.

The work of Wheeler and Johnson, the recent study of the isomeric change of Gabriel's  $\beta$ -chloroethylbenziminooether into  $\beta$ -chloroethylbenzamide by Wislicenus and Körber (*Ber.*, 1902, 35, 164), and, in particular, the isolation by Knorr (*Ber.*, 1897, 30, 922) of *pseudo* (or  $\psi$ )-methiodides of antipyrine and methylquinaldone, and by Knorr and Rabe of an additive compound of benzoyl chloride and methylquinaldone (*loc. cit.*, 927), leaves no doubt that the process of rearrangement of the iminoethers by alkyl iodides is one of addition and subsequent loss of iodide, although attempts to isolate additive compounds of the iminoethers with alkyl iodides and acyl chlorides have proved unsuccessful.

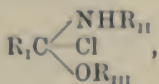
Wheeler and Johnson explain the mechanism of the rearrangement of benziminooethyl ether by the following scheme:



The suggestive work of Stieglitz on the constitution of the salts of iminoethers (*Amer. Chem. J.*, 1899, 21, 101), and the development of the theory of carbonium salts, especially by Kehrman (*Ber.*, 1901, 34, 3815), Baeyer and Villiger (*Ber.*, 1902, 35, 1189), and Gomberg (*Ber.*, 1902, 35, 2397), make it at least probable that the process may be thus formulated:



Following Stieglitz, I am inclined to adopt the structure



instead of  $R_1C \begin{array}{l} \nearrow NR_{II} \\ \text{HCl} \\ \searrow OR_{III} \end{array}$ , for the hydrochlorides of the imino-ethers, although direct experimental evidence has not been forthcoming, except in the case of certain cyclic iminoethers studied by Stieglitz and pupils (*loc. cit.*).

## II. The Rearrangement of Iminoethers by Heat.

The most salient difference between the nitrogen-substituted and :NH iminoethers is observed in their behaviour on heating; the former display considerable stability, whereas the latter give cyanides by loss of alcohol. In this connection, it is of interest to note that semi-oxaliminodiethyl ether, which is known to be rather unstable (Nef, *Annalen*, 1895, 287, 288; *Trans.*, 1901, 79, 702), loses the elements of alcohol on keeping, depositing needles which melt at 165°, and give N = 14.32 per cent. On hydrolysis, an acid melting at 250° is obtained. The compound crystallising in needles is thus identified as ethyl paracyanofornate,  $(CN \cdot CO_2Et)_x$ , which melts at 165° and requires N = 14.1 per cent.

The same decomposition occurs more rapidly on heating the imino-ether.

The first observation of the rearrangement of an iminoether by heat is that of the change of methyl isocyanurate\* into methyl cyanurate produced by boiling (Hofmann, *Ber.*, 1886, 19, 2061).

More recently, the phenomenon has been studied by Wislicenus and Goldschmidt (*Ber.*, 1900, 33, 1470), who observed the change of *N*-phenylformimino-methyl and -ethyl ethers, and of *N*-phenylbenziminomethyl ether into the corresponding substituted amides on heating. Wislicenus and Körber (*Ber.*, 1902, 35, 1991) obtained similar results on heating methoxy- and ethoxy-caffeines.

The isomeric change of isocyanides into nitriles by heating (Weith, *Ber.*, 1876, 9, 454) represents a closely allied case. A considerable number of experiments on the transformation of the recently prepared iminoethers by heat have been carried out. As already indicated (*Trans.*, 1901, 79, 692), *N*-phenylacetiminomethyl ether,  $MeC(OMe):NPh$ , is incompletely rearranged into acetphenylmethanamide by boiling at

\* In accordance with recent researches, cyanuric acid should be formulated as  $(CONH)_3$ , the formula  $(COH:N)_3$  being that of the unknown isocyanuric acid (Hartley, Dobbie, and Lauder, *Trans.*, 1901, 79, 850).



the atmospheric pressure for a few hours, the liquid thereby becoming dark coloured.

Purified *N*-phenylacetiminoethyl ether,  $\text{MeC(OEt):NPh}$  (b. p. 207—208°), after heating in a sealed tube for 5 hours at 220°, was recovered practically unaltered by distilling in a vacuum, the very small residue giving no deposit on adding a fragment of acetphenylethylamide.

By heating *N*-methylbenziminomethyl ether,  $\text{PhC(OMe):NMe}$ , in a sealed tube for 4 hours at 160°, and finally for 2 hours at 200°, no appreciable change could be detected. The substance distilled between 200° and 206° (b. p. of iminoether 203—206°), and was again heated for 9 hours at 250—270°. The resulting product was a viscid, brown liquid, which on distillation was found to contain a small quantity of iminoether, and to consist for the most part of benzdimethylamide, melting at 40—41° after crystallisation from ether and light petroleum. On opening the tube, there was a slight pressure, and a distinct odour of amine was perceptible.

Several experiments were carried out with *N*-phenylbenziminomethyl ether, studied by Wislicenus and Goldschmidt (*loc. cit.*). The compound was prepared from the imide chloride of benzanilide and carefully purified by repeated distillation in a vacuum (b. p. 157—158° under 12 mm. pressure; Wislicenus and Goldschmidt gave 145—150° and 8 mm.). These authors found that by 6 hours' heating at 270—280°, rearrangement occurred to the extent of 35 per cent.

Twenty grams of the iminoether were heated for 8 hours at 240°. There was no pressure, and on distillation the recovered compound boiled at 158—160° under 12 mm. pressure. A sample of the recovered substance, when distilled with steam in dilute hydrochloric acid until free from ethyl benzoate, left no insoluble matter except a little benzanilide. The very small residue left after distillation in a vacuum contained benzanilide, whilst a similar treatment with hydrochloric acid gave rise to a trace of gummy solid.

Ten grams of the iminoether were heated for 8 hours at 250—270°, and then for 3 hours at 300°. On distillation, practically the whole of the material passed over between 150° and 160° under 12 mm. pressure, and rearrangement had certainly not occurred to a greater extent than in the former case.

Sixteen grams of iminoether were heated at 220—230° for 12 hours, and finally at 280—300° for 12 hours. Distillation began at 130°, the temperature rising finally to 177° under 12 mm. pressure, when practically the whole of the material had distilled, leaving a little tarry matter and benzanilide. The boiling point of benzphenylmethylamide is 180—185° under 12 mm. pressure. The greater part consisted of iminoether, as was shown by distilling the whole of the

distillate with dilute hydrochloric acid in a current of steam. But more oily matter remained than in previous experiments, and this, on extraction with ether and crystallisation from ether and light petroleum, proved to be benzphenylmethanamide melting at 55—57°. An accurate estimation of the proportion was not possible, but the quantity certainly did not exceed 1.5 grams.

Even less conclusive results were obtained with *N*-phenylbenziminomethyl ether; no change beyond the formation of a little benzanilide could be detected by heating for 8 hours at 240°.

On heating for 6 hours at 270°, and then for 1 hour at 350°, unchanged iminoether, benzanilide, and ethylene were the only substances that could be detected with certainty.

The decomposition in the sense of the equation  $\text{PhC(OEt):NPh} = \text{PhCO}\cdot\text{NHPh} + \text{C}_2\text{H}_4$  is certainly the main reaction on heating. Nef's explanation (*Annalen*, 1897, 298, 370) of the mechanism of the type of transformation now under discussion, as due to severance and subsequent addition of alkylene, has been already criticised by Wislicenus and Goldschmidt (*loc. cit.*), and is rendered additionally improbable by the above result.

After 20 hours' heating at 250—260°, removal of unchanged iminoether by distillation, and hydrolysis of the residue with alcoholic potassium hydroxide, a small quantity of secondary amine was detected, by the formation of nitrosamine, in the liberated base, which consisted chiefly of aniline. So far, this is the only positive evidence of isomeric change of an ethyl iminoether which I have succeeded in obtaining.

The results recorded here cannot be regarded as satisfactory in demonstrating the rearrangement by simple heating. In accordance with my other experiments on the isomeric change of iminoethers, they show that in these compounds the methyl group is more labile than the ethyl. This result is contrary to the experience of Wislicenus and Goldschmidt, who, under similar conditions, found a 65 per cent. rearrangement of *N*-phenylformiminomethyl ether as compared with a 40 per cent. transformation of the methyl analogue.

It is open to doubt that the isomeric change of iminoethers on heating is a simple reaction, and it remains to be proved that the secondary changes which inevitably accompany reactions carried out at a high temperature play no part in the change. In many instances, other products have been noted; thus, diphenylformamidine arises during the transformation of *N*-phenylformiminomethyl ether, as recorded by Wislicenus and Goldschmidt; the rearrangement of the alkyloxycaffeines, studied by Wislicenus and Körber, leads to the simultaneous formation of amines, and a similar result has been obtained in the case of *N*-methylbenziminomethyl ether (*vide supra*).

Although the alkyl iodides are the most suitable catalytic agents

for inducing the isomeric change of the iminoethers, they are probably not the only ones available.

The work of Wade (Trans., 1902, 81, 1603) on the isomeric change of the *isocyanides* on heating has demonstrated the necessity of a catalytic agent for that class of substances. It is not unlikely that future experiments may lead to the same conclusion in the case of the iminoethers.

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## XLVII.—*The Nature and Probable Mechanism of the Replacement of Metallic by Organic Radicles in Tautomeric Compounds.*

By G. D. LANDER.

ALKYLATION by means of dry silver oxide and alkyl iodides has greatly extended the application of the method of substitution depending on the use of silver salts. Most of the recent work bearing on Purdie and Pitkeathly's reaction, which I have recorded in this Journal (Trans., 1902, 81, 591, and preceding papers), has been undertaken in the hope of obtaining fresh experimental data, and, if possible, of shedding fresh light on the involved problem of the mechanism of the replacement of the metallic radicle in tautomeric compounds. As, hitherto, I have avoided discussing the theoretical bearings of much of this work, I now propose to review the experimental results and to attempt to test them in the light of current theories on the mechanism of this replacement.

A complete demonstration of any theory devised for the explanation of these phenomena is necessarily impossible, so long as that theory rests on the assumption of intangible intermediate stages in a reaction. The arbitrary character of the additive hypothesis as applied to these phenomena, to which attention has already been drawn by Wislicenus (*Tautomerie, Ahrens-Sammlung*, 1897, 252), leads me to suggest that the merits of a theory based on the display of tautomerism by compounds containing metallic radicles deserve careful consideration.

The recent work of Titherley and of Hantzsch, to which reference is made in the sequel, renders this assumption more probable than was formerly the case.



I. *Review of Experimental Data.*

(i) *The Substituted Amides.*—Ethylation of the substituted amides by dry silver oxide and ethyl iodide is, in general, sharply distinguished from the analogous methylation in that, under similar conditions, the former process yields iminoethers,  $\cdot\text{C}(\text{OEt})\cdot\text{N}\cdot$ , almost exclusively, whilst the latter reaction leads to the simultaneous production in variable proportions of iminoether and isomeric substituted amide,  $\cdot\text{C}(\text{OMe})\cdot\text{N}\cdot$  and  $\cdot\text{CO}\cdot\text{NMe}\cdot$ .

For brevity, I propose to refer to this type of methylation as 'anomalous,' and, similarly, to describe other reactions involving the replacement of metallic radicles in which isomerides are formed as 'anomalous replacements,' but no theoretical significance is attached to these expressions.

The anomaly in the instance under discussion is only apparent, for when acetanilide is ethylated by means of dry silver oxide and ethyl iodide in a closed vessel at  $100^\circ$ , both ethyl homologues,  $\text{PhN}:\text{C}(\text{OEt})\text{Me}$  and  $\text{PhNEt}\cdot\text{COMe}$ , are produced, the process resembling the methylation of the same amide in an open vessel at  $40$ – $50^\circ$ . Under the former conditions, ethylation is comparable with methylation.

'Anomalous' alkylation of this type was observed by Friedländer and Weinberg (*Ber.*, 1882, 15, 1421), who obtained mixtures of *N*- and *O*-homologues of carbostyryl from its sodium derivative and ethyl iodide. Ponomarew (*Ber.*, 1885, 18, 3271) showed that silver cyanurate, which, with alkyl iodides at low temperatures, yields *O*-ethers, furnishes mixtures of *N*- and *O*-compounds in closed vessels at  $100^\circ$ .

With silver formanilide and ethyl iodide at  $100^\circ$ , Wheeler and Johnson (*Amer. Chem. J.*, 1900, 23, 136) observed the formation of the *N*-derivative alone, whereas the *O*-compound was the main product of reaction at lower temperatures in an open vessel.

(ii) *The Keto-enol Compounds.*—The results of ethylation by means of dry silver oxide of malonic, ethylacetoacetic, acetoacetic, and benzoylacetic esters have been previously recorded (*Trans.*, 1900, 77, 729; *Proc.*, 1901, 17, 59), the analogous ethylation of ethyl oxaloacetate being described below (p. 417).

The study of the substitution of alkyl groups for sodium and silver in the keto-enol compounds shows that generally the replacement of silver occurs most readily in those compounds in which the replacement of sodium takes place with greatest difficulty and *vice versa*.

Moreover, the ease with which silver undergoes replacement is correlated with the stability of the enol form, that is, with the development of acidic functions.

Thus, ethyl malonate, ethyl ethylacetoacetate, ethyl acetoacetate, and

the corresponding benzoylacetate readily undergo the sodium-alkyl replacement, yielding *C*-esters; the silver-alkyl reaction occurs, however, with greater difficulty with ethyl malonate and ethyl ethylacetoacetate, the product being also *C*-ester, and only in the case of the last two esters, which readily undergo silver-alkyl replacement, is any appreciable amount (about 5 per cent.) of the *O*-ester formed.

Ethyl oxaloacetate, on the other hand, is alkylated to the *C*-ester with difficulty by the sodium-alkyl reaction, whereas it readily undergoes the silver-alkyl replacement yielding the *O*-ester exclusively, the latter result being likewise attained by the alkylation of its silver derivative.

In this respect, the silver derivative of ethyl oxaloacetate resembles the silver salts of the carboxylic acids; these readily react with alkyl iodides, and thereby differ from their sodium salts, which do so with greater difficulty.

The distinction between the two modes of replacement is not, however, always so sharply defined; thus the alkali (in alcoholic solution) and silver derivatives of oxymethylenecamphor both readily undergo replacement of the *O*-type (Bishop, Claisen, and Sinclair, *Annalen*, 1894, 281, 317), a behaviour which resembles that of the phenols.

Amongst the keto-enol compounds, 'anomalous alkylation' through the agency of a sodium compound appears to be unknown, and first appears with silver acetylacetone (Nef, *Annalen*, 1893, 276, 217) and the silver oxide alkylation of ethyl acetoacetate and benzoylacetate. This class of compound is generally characterised by 'anomalous acylation,' the introduction of the  $\text{CO}_2\text{Et}$  group into ethyl acetoacetate (Claisen, *Ber.*, 1892, 25, 1760) and of the acetyl and benzoyl radicles by the action of the respective chlorides on the copper derivative of ethyl acetoacetate (Nef, *Annalen*, 1891, 266, 110) being cases in point.

## II. Does the Silver Oxide Reaction afford a Valid Basis for a Theoretical Discussion of the Replacement of Metallic Radicles?

Before the results indicated in the preceding section can be discussed from any theoretical point of view, it is very important to decide whether the alkylation, as carried out by the silver oxide reaction, is comparable with that which would occur between the isolated silver derivative and an alkyl iodide.

In the alkylation by silver oxide, the salt is rapidly decomposed by the iodide, indeed, the process may be loosely described as 'nascent alkylation,' and might differ from ordinary alkylation. Few stable silver salts of the keto-enol compounds and substituted amides are known, but the silver derivatives of ethyl oxaloacetate (Nef,

*Annalen*, 1893, 277, 73) and silver formanilide (Comstock and Kleeberg, *Amer. Chem. J.*, 1891, 13, 514) can be prepared, and give *O*-derivatives with alkyl iodides. The corresponding alkylation by silver oxide was therefore examined.

*Ethylation of Ethyl Oxaloacetate by means of Dry Silver Oxide.*—Forty grams of dry silver oxide were added in small portions to a solution of 30 grams of ethyl oxaloacetate and 56 grams of ethyl iodide; the somewhat violent reaction is at first moderated by cooling and then completed by boiling for half an hour on the water-bath. After 12 hours, the mixture was fractionated in a partial vacuum. A small fraction distilled between  $130^{\circ}$  and  $140^{\circ}$  under 17 mm. pressure and the main bulk of the liquid between  $134^{\circ}$  and  $142^{\circ}$  (11–12 mm.), leaving a considerable residue. Neither distillates nor residue gave a coloration with alcoholic ferric chloride. The whole distillate (21 grams) was shaken with dilute potassium hydroxide, when no ester dissolved, and, on distillation, 19.5 grams were recovered, of which the chief fraction (13 grams) boiled at  $135$ – $137^{\circ}$  under 11 mm. pressure, the extreme boiling points being  $135^{\circ}$  under 12 mm. and  $138^{\circ}$  under 11 mm. pressure:

0.124 gave 0.2523  $\text{CO}_2$  and 0.085  $\text{H}_2\text{O}$ .  $\text{C} = 55.5$ ;  $\text{H} = 7.6$ .

$\text{C}_{10}\text{H}_{16}\text{O}_5$  requires  $\text{C} = 55.55$ ;  $\text{H} = 7.4$  per cent.

The product evidently consisted of ethyl ethoxyfumarate, and therefore the alkylation by the silver oxide method is similar to that by the silver salt.

*Methylation of Formanilide by means of Dry Silver Oxide.*—Thirty-five grams of dry silver oxide were added gradually to a slightly warm solution of 12 grams of formanilide in 42 grams of methyl iodide. After about one-third of the oxide had been added, the mixture was diluted with ether and finally boiled for 2 hours. On distillation, the main product, consisting of 9.2 grams of *N*-phenylformiminomethyl ether, boiled at  $86$ – $90^{\circ}$  under 13 mm., and at  $194$ – $198^{\circ}$  under the ordinary pressure. The residue, on further distillation, yielded a small quantity of brown oil, having the odour of a cyanide and boiling between  $280^{\circ}$  and  $290^{\circ}$  under the ordinary pressure. When hydrolysed by alcoholic potassium hydroxide, this oil gave a secondary base, showing that the isomeric amide had also been formed to a slight extent. A small quantity of diphenylformamidine (m. p.  $131$ – $133^{\circ}$ ) was also present in the product of reaction.

In a comparative experiment carried out by boiling 21.5 grams of silver formanilide suspended in ether with 17 grams of methyl iodide for 3 hours, the yield of iminoether amounted to only 4 grams; there was also more isomeric amide (the formation of which does not appear to have been noted by Comstock and Kleeberg) and considerably more



diphenylformamidine than in the silver oxide methylation. Although these differences are important, the results of the two syntheses are comparable.

As a result of these experiments, the question propounded in this section may be answered in the affirmative.

### III. *Hypotheses Employed in Explaining the Replacement of Metallic Radicles.*

(i) *The Addition Hypothesis.*—Of the hypotheses which have been proposed in explanation of the reactions of tautomeric compounds and their metallic derivatives, that of addition (Michael, *J. pr. Chem.*, 1883, 37, 486; Nef, *Annalen*, 1891, 266, 59) has found very general acceptance, particularly when intermediate additive compounds can be isolated. But among the metallic derivatives of tautomeric compounds the additive compound of acetyl chloride and ethyl mercuriacetoacetate (Nef, *Annalen*, *loc. cit.*) is, as far as I am aware, the only example which has hitherto been isolated in a pure state. When the substitution occurs in a single direction, the formation of either product can be equally well explained by taking one or other of the two possible structures of the metallic derivative. When, however, 'anomalous replacement' occurs, additional assumptions are necessary, such as that of the simultaneous occurrence of direct and indirect reactions, these involving still further suppositions to decide when direct and indirect replacements shall occur, and which shall predominate. The positive-negative theory of Michael (*J. pr. Chem.*, 1892, 46, 205) attempts this task, but relative positivity and negativity alone can hardly account for the difference between the methylation and ethylation of the substituted amides by means of silver oxide.

In view of the doubly unsaturated character of the cyanides, an explanation of the reactions of the metallic cyanides on the assumption of intermediate addition is more probably correct than in other cases. Setting aside the possibility of direct interchange, Wade has recently (*Trans.*, 1902, 81, 1611) put forward a modified addition hypothesis, which satisfactorily accounts for cyanide reactions owing to the possibility of addition occurring in at least two ways. But the hypothesis is restricted in scope to the cyanides. Its extension to the cases of the formation of nitromethane and methyl cyanate by Wade (p. 1612) is inadequate, for methyl nitrite is formed as well as nitromethane (Bewad, *J. Russ. Phys. Chem. Soc.*, 1892, 1, 125), and cyanic acid is not typical of the  $\cdot\text{CO}\cdot\text{NH}\cdot$  compounds, for its *O*-esters are unknown (Nef, *Annalen*, 1895, 287, 265). In the majority of cases of 'anomalous replacement,' *O*-derivatives are formed, and it is difficult to see how their production by additive processes can be explained,

except on the assumption of the quadrivalency of oxygen, which, in spite of its manifestation in the oxonium salts, can scarcely, at present, be assumed for a large class of compounds containing metallic radicles.

(ii) *The Possibility of Isomeric Change of the Compounds*  $\cdot\text{C}(\text{OR})\cdot\text{N}\cdot$  or  $\cdot\text{C}(\text{OR})\cdot\text{C}\cdot$ .—Catalytic transformation of the iminoethers in accordance with the scheme  $\cdot\text{C}(\text{OR})\cdot\text{N}\cdot \rightarrow \cdot\text{CO}\cdot\text{NR}\cdot$  (catalyser = RI) would satisfactorily account for this class of 'anomalous replacements,' and, in view of its readier occurrence with methyl than with ethyl compounds (compare preceding paper), would further explain the difference between methylation and ethylation under similar conditions. Although at first sight this seemed a very probable explanation, I am inclined to regard it as inadequate on the following grounds.

(a) At temperatures between  $40^\circ$  and  $50^\circ$ , acetanilide gives, on silver oxide methylation, a mixture of *N*-phenylacetiminomethyl ether,  $\text{PhN}\cdot\text{C}(\text{OMe})\text{Me}$ , and the isomeric substituted amide, and a similar result is obtained by methylation in benzene solution during a week at the ordinary temperature.

(b) *N*-Phenylbenziminomethyl ether is produced along with the isomeric amide by methylation of benzanilide by silver oxide in boiling benzene solution, but when the pure iminoether is boiled with silver oxide, methyl iodide, and benzene for 4 hours it does not undergo transformation.

(c) Although 'anomalous ethylation' of acetanilide occurs in a closed vessel at  $100^\circ$ , *N*-phenylacetiminoethyl ether is practically unaltered by 15 hours' heating with ethyl iodide at that temperature (compare preceding paper).

(d) The *N*-phenylformiminoethers would appear, from the work of Wislicenus and Goldschmidt (compare preceding paper), to undergo rearrangement at least as easily as the *N*-phenylacetimino- and other imino-ethers, yet 'anomalous methylation' is not so characteristic of formanilide as of other substituted amides.

These observations, whilst they do not absolutely exclude this explanation, nevertheless render it very improbable. It might, for example, be supposed that isomeric change after formation is not necessarily so easy as at the moment of formation, and an explanation in these terms might be given. But it could have no value, for it avoids the issue, unless the mechanism, to which such a phenomenon is due, were elucidated.

An explanation of 'anomalous alkylation' of keto-enol compounds by the supposition of change of the grouping  $\cdot\text{C}(\text{OR})\cdot\text{C}\cdot$  into  $\cdot\text{CO}\cdot\text{CR}\cdot$  is less tenable than with the substituted amides, for the ethoxycrotonic and ethoxyfumaric esters have not been transformed (Wislicenus and Goldschmidt, *Ber.*, 1900, 33, 1469), and in the nearest allied case of the phenylvinyl ethers, which change on super-

heating into homologues of acetophenone, the higher alkyl radicles show greater mobility than the lower (Claisen, *Ber.*, 1896, 29, 2932).

'Anomalous acylation' may, however, be found to admit of an adequate explanation by the assumption of isomeric change after formation, for Claisen and Haase (*Ber.*, 1900, 33, 3780) have shown that ethyl *O*-acetylacetoacetate changes with ease into the *C*-acetyl compound on treatment with alkaline substances.

(iii) *The Desmotropic Change of Momentarily Free Tautomeric Residues.*—The views on the substitution of metallic radicles developed by Wislicenus (*Tautomerie, Ahrens-Sammlung*, 1897, 249, *et seq.*), are of such importance that a summary may not be superfluous.

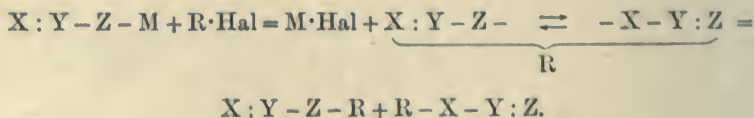
It is assumed that the metal is attached in the stable salts to the most electronegative atom available. 'Direct' replacement, in which the entrant radicle takes the same place as the metal atom, occurs under a certain 'constraint' ('*Zwang*'). 'Indirect' or 'free' replacement is that in which the entrant radicle assumes a different, and more favoured, position to that of the metallic atom. The physical conditions are laid down under which each of these types of reaction may be expected to occur.

1. *For a constrained ('Zwang') reaction*:—Use of an insoluble derivative, preferably a silver compound; avoidance of a large excess of solvent, particularly if this is a dissociating medium; a low temperature.

2. *For a 'free' reaction*:—Use of a soluble (alkali) derivative; a dissociating medium (water, alcohol); an elevated temperature.

The two constitutive factors, dependent on the tautomeric and entrant residues, are of great importance, and a variation can only be expected as the result of constitutive influences of uncommon strength.

Regarding the formation of metal halide as the first step in replacement, there may very well be produced free residues, and desmotropic change may occur all the more readily as there is no attendant transport of atoms. If time be allowed for this change, we have a 'free' reaction. Diagrammatically, this view of the mechanism of replacement may be expressed by the scheme:



The silver oxide alkylations offer a suitable experimental basis for testing these issues. All the conditions of a 'constrained' reaction are easily realisable in them, and the results of the alkylation of the substituted amides are generally in accordance with Wislicenus' principles. But the formation of more than 90 per cent. of *C*-ethyl-



homologues in the alkylation of ethyl acetoacetate and benzoylacetate is scarcely in harmony with them. As Wislicenus has, however, pointed out, constitutive influences are of prime moment. The study of the 'constrained' alkylation of these esters would lead us to conclude that, in the corresponding salts, the metal is attached to carbon, or else that constitutive influences of 'an uncommon kind' are at play. To attribute the phenomena to such influences is, however, to avoid the issue, so long as we are in ignorance of the nature of these influences. It is at least difficult to see why the 'constrained' conditions of a silver oxide alkylation should lead to results similar in kind to those of a sodium alkylation under free conditions.

Setting aside the addition hypothesis, which could very probably, by suitable alterations of an empirical and formal character, be made to apply to all the facts for which an explanation is required, the more or less complete inadequacy of other modes of elucidation has led me to seek in the existence of tautomeric metal salts, a simple explanation of the facts of the replacement of metallic radicles.

#### IV. *The Possibility of the Reaction of Metallic Derivatives in Tautomeric Forms.*

The distinction between the hypothesis of momentarily free valencies and that of the reaction of metallic derivatives in tautomeric forms is very slight. Regarding the process of desmotropic change as essentially dependent on dissociation, the difference between the two hypotheses amounts to the choice as to which of the two systems, tautomeric residue and metallic atom, or tautomeric residue and organic residue, is more likely to be capable of existence. All our experience of ionic dissociation favours the probability of the existence of the former rather than of the latter system. A metallic atom more easily undergoes ionic separation from an acid residue than hydrogen, and, in spite of the large atomic weight, is probably very mobile. Dissociation to any important degree of a compound of two organic residues, such as an ester, does not occur. To admit the possibility of the existence of the system, tautomeric residue and metal atom, is tantamount to accepting the possibility of the existence of the desmotropic metal salt, for the salt reacts as though it possessed two structures. If, as Brühl (*Ber.*, 1899, 32, 2329) and, more recently, Lapworth and Hann (*Trans.*, 1902, 81, 1508) suppose, the display of desmotropy depends on ionic dissociation, and, as the latter authors have shown both desmotropic radicles must be ions, the conclusion that a metallic salt in solution may exist in desmotropic forms is almost inevitable, for that ionic dissociation upon which desmotropy depends will be greater with the metallic derivative than with the parent hydrogen compound.

The structure in solution has no connection with that of the solid salt. If the latter is a well-defined, crystalline substance, it must possess a definite structure (Knorr, *Annalen*, 1899, 306, 345), and no doubt the metal is usually attached to the most electronegative atom available. But when it passes into solution, and it is very probable that all salts, even the sparingly soluble silver salts, must do so before entering into reaction, an allelotropic mixture will be formed (Knorr, *loc. cit.*, 344). The proportion of the two desmotropic isomerides present in that mixture at the time of reaction must vary and depend on all the conditions, physical and constitutive, and on these factors the nature of the stable products must depend. The present hypothesis differs from that of Pechmann (*Ber.*, 1892, 25, 1042), who seems to have supposed that the salts of ethyl acetoacetate contain the metal attached to carbon alone, only in the postulate that, whatever be the structure of the solid salt, the dissolved substance is likely to display allelotropism, that is, it differs from Pechmann's view just as our present conceptions of tautomeric phenomena differ from those current at that time (1892).

Perhaps the chief objection to the supposition of desmotropic metallic compounds is the very general belief that a metallic atom must be attached to oxygen (or some other electronegative element). That this is not necessarily the case was foreshadowed by Titherley's observation (*Trans.*, 1901, 79, 409) of labile silver derivatives of benzamide and acetamide, and has been decisively negated by Hantzsch's isolation of isomeric mercuric cyanurates (*Ber.*, 1902, 35, 2717). A reaction in solution and an elevated temperature (the conditions of a 'free' reaction) seem always to lead to carbon (or nitrogen) replacement, and involve the supposition that in the majority of cases the most favoured position of the metal atom is in attachment with those elements. This conclusion is borne out by the experiments of Hantzsch (*loc. cit.*), in which the salt  $[(\text{CO}\cdot\text{N})_2\text{Hg}]_3$  is precipitated from solutions of sodium cyanurate at 100°.

It is also not unlikely that, in the silver oxide alkylation of the keto-enol compounds studied, the nature and approximate proportions of the salts directly formed are roughly the same as those of the desmotropic hydrogen compounds. Alkylation, therefore, throws light on the constitution of the latter substances, a possibility indicated by Wislicenus (*Tautomerie*, 254).

The silver oxide alkylation of the substituted amides brings out in a clear manner the prime importance of conditions. Ethylation indicates that the salt in the first instance is almost entirely of the type  $\cdot\text{C}(\text{OAg})\cdot\text{N}\cdot$ , very little of the desmotropic  $\cdot\text{CO}\cdot\text{NAg}\cdot$  being present. The 'anomalous alkylation' of these substances affords a remarkable illustration of the importance of each of the factors recognised by Wislicenus as determining the nature of the replacement of metal.

The greater the acidity of the CONH compound, the less readily will the desmotropic nitrogen salt be formed, in conformity with which we find that formanilide and the cyclic amides, which form stable silver derivatives, undergo 'anomalous methylation' to a less extent than the amides, which do not form such silver compounds.

The relative facility of 'anomalous methylation' depends, firstly, on the constitutive factor contributed by the entrant group, the smaller methyl group entering more readily into the *N*-position than the larger ethyl radicle; secondly, on the constitutive factor due to the orientation of the aryl group attached to nitrogen, as shown by a comparison of the methylation of aceto-*o*-toluidide with that of aceto-*p*-toluidide (Trans., 1901, 79, 694, 696). The difference between methylation and ethylation is stereochemical. The occurrence of 'anomalous ethylation' at higher temperatures is due to the readier occurrence of desmotropic change in the salt and to a diminished operation of the stereochemical influences.

According to the hypothesis of the reaction of desmotropic salts, the processes of sodium and silver replacement by alkyl radicles are essentially similar; the differences observed in the result are due to the dissimilar conditions under which these metallic derivatives are employed in synthetical operations and to the greater ease of replacement of the silver radicle which generally obtains in the *O*-salts.

Under 'constrained' conditions, the replacement of sodium by alkyl is either at a minimum, as in the case of ethyl oxaloacetate (Wislicenus and Arnold, *Annalen*, 1888, 246, 337), or non-existent. I have been unable, for example, to detect any replacement of sodium on boiling anhydrous ethyl sodioacetoacetate with ethyl iodide in light petroleum solution.

Any speculation on the mechanism of the replacement of metallic radicles must, however, remain hypothetical until either definite intermediate additive compounds have been isolated and the reaction then carried to its termination—which does not appear to have been done with Nef's additive compound of acetyl chloride and ethyl mercuriacetoacetate—or until isomeric metallic derivatives have been prepared in greater number and caused to enter into these reactions of replacement.

The expense of the experimental work of this and the preceding paper was defrayed by a grant from the Research Fund Committee of the Chemical Society, for which I desire to express my indebtedness.

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# XLVIII.—*The Biological Method for Resolving Inactive Acids into their Optically Active Components.*

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THE method for resolving inactive substances into their optically active components by the selective action of micro-organisms was first employed by Pasteur in the classical example of racemic acid, and has occasionally been used since his time for the preparation of one of the active forms. In much of the research in this field no attempt was made to work with pure cultures. Hence, although the optically active products desired were in certain cases successfully obtained, there is often considerable doubt as to the exact organism by which the resolution had actually been effected, the object having been to obtain the pure active isomeride rather than to examine the action of any particular organism upon the inactive form; thus, for example, a resolution ascribed to *Penicillium glaucum* may often have been accomplished not by that mould but by the bacteria with which the solution under investigation had accidentally become contaminated (compare Landolt, *Das optische Drehungsvermögen*, 1898, 63). Le Bel clearly indicates that his experiments on the resolution of inactive substances by the biological method were not conducted under conditions which excluded the presence of organisms other than the one originally sown in the solution, when he writes, "Von Sterilisiren durch die Wärme und Cultiviren in geschlossenem Raum liess ich ab, weil man die Substanz beständig untersuchen und bearbeiten muss, und weil ich mehrmals während der Cultur beobachtete, dass die Luft neue Sporen gebracht hatte, die besser wuchsen als der schon entwickelte Pilz" (*Ber.*, 1900, 33, 1006).

Little is known as to the general mechanism of the change during the growth of organisms on inactive substances, and particularly as to the ratio, which the amount of active product obtained bears to that of inactive substance decomposed. Two possible cases may be distinguished:

(1) Only one of the active constituents is attacked, whilst the other is untouched. The amount of active constituent remaining is in this case equal to half the substance resolved, but it may be mixed with more or less of the original *i*-substance, according to the experimental conditions. E. Fischer and Thierfelder (*Ber.*, 1894, 27, 2031) have found, for instance, that various species of yeast readily ferment *d*-mannose but have no action on *l*-mannose. Further, ordinary

brewers' yeast has been used by E. Fischer to resolve *i*-glucose, *i*-mannose, *i*-fructose, and *i*-galactose (*Ber.*, 1890, 23, 382, 2620; 1892, 25, 1259), and the well-known hypothesis of lock and key has been proposed with reference to these results. The experiments of Frankland and Frew indicate that their resolution of glyceric acid may most probably be classified under this same heading, as *i*-calcium glycerate is attacked by *Bacillus ethaceticus* in such a manner that the *d*-salt is completely decomposed and the *l*-salt is left untouched and can be quantitatively extracted (*Trans.*, 1891, ~~50~~<sup>59</sup>, 81, 96).?

(2) Both active constituents are simultaneously attacked but at different rates. In this case, the amount of active constituent remaining must be less than half that of the substance resolved.

With regard to the resolution of inactive substances by moulds, it is as yet uncertain under which heading it is to be placed. The prevailing opinion, first expressed by Pasteur in his "*Recherches sur la dissymétrie moléculaire des produits organiques naturels*," appears to be that it belongs to case (1) (compare Landolt, *loc. cit.*, pp. 63, 99; Schulze and Bosshard, *Zeit. physiol. Chem.*, 1886, 10, 141; Purdie and J. W. Walker, *Trans.*, 1893, 63, 229). From Pasteur's description of the resolution of ammonium racemate by *Penicillium glaucum* (*Compt. rend.*, 1860, 51, 298) it is not clear, however, whether half the inactive salt had actually been decomposed, although it is stated that the *l*-acid may easily be isolated. On the other hand, Schulze and Bosshard point out that more than half the original substance had been used up during the growth of the mould, but the experimental evidence submitted by those investigators is insufficient to determine in which of the two foregoing classes the resolution of *r*-leucine and *r*-glutaminic acid attained by them is to be assigned. Pfeffer (*Jahrbücher wissenschaft. Botanik*, 1895, 221) has observed that in the decomposition of racemic acid by various moulds both the *d*- and *l*-isomerides were invariably attacked, the rates being in some cases identical, whilst in others the *d*- was more rapidly attacked than the *l*-acid.

The experiments described in this paper were carried out with the object of ascertaining the mode of action of various moulds on a series of *i*-acids, with special reference to the question whether the organism acts on one of the constituents exclusively or on both at different rates. Two additional points were kept in view: firstly, whether from the action of organisms any definite relationship could be established between the configuration of the various related acids, and, secondly, whether the active products of the action of different organisms on the same series of acids show any regularity as to sign of rotation. The experiments were conducted mainly with *Penicillium glaucum*, Link, *Sterigmatocystis nigra* (van Tieghem) (= *Aspergillus niger*, van

Tieghem, *olim*), and *Aspergillus griseus*, Link,\* special precautions being taken to ensure that the various cultures were pure and that the aqueous solutions of inactive substances employed were sterile before they were inoculated with the pure culture. The solutions were either neutral or faintly acid. Raulin's solution *minus* the sugar and tartaric acid (Flügge, *Mikro-organismen*, p. 109) served in the majority of cases as the inorganic nutrient material. After inoculation, the solutions were protected from contamination by plugs of cotton wool. The growths of the *Penicillium* were conducted at 22°, those of the yeasts at 25°, and of the others at 37°. When the growths had ceased, the respective solutions were filtered, concentrated by evaporation, clarified whenever necessary by animal charcoal, and examined. It should be mentioned that the isolation of the pure active isomerides was in no case attempted. In cases where the resolution was slight and where the inactive solid substance was an *r*-compound and not a *dl*-mixture, the activity of the product was often rendered more apparent by withdrawing from solution a crop of the *r*-compound, the active constituent remaining in the mother liquor.

### Racemic Acid.

*Penicillium glaucum*, *Aspergillus niger*, and *Aspergillus griseus* were grown on separate solutions of ammonium racemate. In all cases there was a good growth of mycelium with little sporing. The rotation of the concentrated solution of ammonium salt was observed in each case, whilst the concentration was determined by weighing the acid, obtained by conversion of the ammonium salt into the lead salt and decomposition of the latter by hydrogen sulphide.

| Original acid.          | Volume of solution. | Duration of growth. | Acid recovered. | $[\alpha]_D$ of ammonium salt. |
|-------------------------|---------------------|---------------------|-----------------|--------------------------------|
| <i>P. g.</i> 7.52 grams | 200 c.c.            | 5 months            | 4.3 grams       | -4.1°                          |
| <i>A. n.</i> 3.76 "     | 100 "               | 3½ "                | 1.3 "           | 7.2                            |
| <i>A. gr.</i> 3.76 "    | 100 "               | 3½ "                | 1.3 "           | 6.1                            |

As ammonium *d*-tartrate has  $[\alpha]_D$  34.26° ( $c = 9.433$ ), it is obvious that the *d*- and *l*-salts are attacked at different rates, the *d*-salt being attacked more readily than its isomeride. It is probable that in Pasteur's classical experiment (*loc. cit.*), a much more highly active product had resulted than in the above instance, since Pasteur states

\* Our thanks are due to the Director of Kew Gardens for kindly naming these cultures.



that he was able to separate the *l*-acid with ease. Our results with *P. g.* and *A. n.* corroborate those of Pfeffer (*loc. cit.*).

### *Dimethoxysuccinic Acid.*

The acid was obtained from its methyl ester prepared by alkylating methyl racemate by silver oxide and methyl iodide, as described by Purdie and Irvine for the *d*-compound (Trans., 1901, 79, 957).

*P. g.*—Ammonium salt from 1 gram of acid; 100 c.c.; feeble growth;  $3\frac{1}{2}$  months; solution when evaporated to 25 c.c. gave  $\alpha_D -0.05^\circ$  ( $l=4$ ). In a second experiment, a similar result was obtained. In a third experiment, 5 grams of barium salt were used in 670 c.c.; feeble growth;  $3\frac{1}{2}$  months; solution was concentrated and 2 grams of salt were withdrawn. The filtrate, made up to 25 c.c. gave  $\alpha_D -0.05^\circ$  ( $l=4$ ), the total salt recovered being 4 grams. As the active barium dimethoxysuccinate has been shown by Purdie and Irvine to have  $[\alpha]_D 27.22^\circ$ , the *d*- and *l*-forms were apparently attacked by *P. g.* at almost equal rates.

*A. n.*—A solution of 5 grams of barium salt in 670 c.c. showed a considerable growth in four months. After removal of 2.4 grams, the filtrate (25 c.c.) gave  $\alpha_D -0.12^\circ$  ( $l=4$ ).

With *A. gr.* the observed rotation was also slightly lævorotatory.

### *Lactic Acid.*

Lewkowitsch (*Ber.*, 1883, 16, 2720) found that an acidified solution of ammonium lactate became dextrorotatory when *P. g.* was grown on it, and Linossier (*Bull. Soc. chim.*, 1891, [3], 6, 10), by growing the same mould on ammonium lactate, prepared a lævorotatory zinc salt. These results are concordant, as the rotation of the active lactic acids is of the opposite sign to that of their inorganic salts. Frankland and MacGregor (Trans., 1893, 63, 1028) have also obtained a partial resolution of calcium lactate by bacterial fermentation.

*P. g.*—Twenty-five c.c. of *N*-lactic acid solution (2.25 grams) were neutralised by aqueous potassium hydroxide and made up to 600 c.c. There was a good growth of mycelium and spores. After 2 weeks, the residual lactic acid was estimated in an aliquot portion of the solution by extracting the acidified solution with ether, converting the acid into zinc salt, and estimating the concentration of this. The total lactic acid remaining amounted to 1.571 grams, so that the acid, which had been attacked, was 0.679 grams. A small crop of inactive salt was removed from the zinc salt, which then gave  $\alpha_D -0.31^\circ$ ,  $l=4$ ,  $c=4.016$ ,  $[\alpha]_D -1.93^\circ$ . The solution measured 26 c.c. Since  $[\alpha]_D$  of pure active zinc lactate is  $7.74^\circ$  for a similar concentration, it follows that the total active salt

present in the above solution was 0.2604, the total amount in the original solution being 0.296 grams, corresponding with 0.219 grams of lactic acid. Hence,  $0.679 + 0.219 = 0.898$  grams of inactive acid were resolved and yielded only 0.219 grams of active acid, or 24.4 per cent.

It follows that in this case the *d*-acid was attacked about twice as rapidly as the *l*-isomeride.

*A. n.* sown into 500 c.c. of a 5 per cent. solution of ammonium lactate yielded a large growth of mycelium and abundant sporing. After seven weeks, the acid present was extracted and converted into zinc salt, from the aqueous solution of which a crop of the *r*-salt was withdrawn, whilst the filtrate gave  $[\alpha]_D - 1.8^\circ$  ( $c = 2.18$ ) and, when acidified, became dextrorotatory.

*A. gr.* also grew well in a similar solution. After five weeks, the solution was treated as in the preceding experiment; the solution of zinc salt gave  $[\alpha]_D - 3.5^\circ$  ( $c = 2.72$ ), and changed its sign on being acidified.

*Bacillus subtilis* was cultivated in a similar solution. After 10 weeks the solution was acidified and the volatile acids present were removed by steam distillation. The residual lactic acid was extracted with ether and converted into barium salt, an aqueous solution of which gave  $\alpha_D + 0.27^\circ$  ( $l = 2$ ), the  $[\alpha]_D$  being only  $0.4^\circ$ ; the change of sign after acidification was also noted.

A species of *Chaetophoma*, isolated from the air of the laboratory, was grown on potassium lactate solution and the product converted into the zinc salt, which was distinctly lævorotatory.

*Saccharomyces ellipsoideus* and *Sacch. cerevisiae* when grown on potassium lactate solution both yielded lævorotatory salts, the amount of active acid in each case forming only a small proportion (10–5 per cent.) of the total acid decomposed.

#### Alanine.

E. Fischer (*Ber.*, 1899, 32, 2459) found that *P. g.* grew badly in a 2 per cent. solution of alanine, whilst a better growth was obtained with *A. n.* In the latter case, 10 per cent. of the original *r*-alanine was attacked, and the product, examined as the hydrochloride, was slightly lævorotatory. Fischer, accordingly, obtained the active alanines by resolving *r*-benzoylalanine by alkaloids. We found that a fairly marked resolution of alanine might be obtained by mould-growth. It should be noted that active alanine itself is very slightly active, but the *l*-hydrochloride, according to Fischer, has  $[\alpha]_D - 9.68^\circ$  ( $c = 9.2996$ ). In the light of the latter determination, the rotations obtained in the following experiments are abnormally high.

*P. g.* grew well on a solution containing 5 grams of alanine in 1000 c.c. After 4 weeks, 1.1 gram were recovered and converted into hydrochloride, a determination of the specific rotation of which gave  $l=1$ ,  $c=12.92$ ,  $\alpha_D - 0.48^\circ$ ,  $[\alpha]_D - 3.7^\circ$ .

A solution of 5 grams of the base in 280 c.c. when sown with *A. n.* gave a large growth with much sporing. After 3 weeks, 4.2 grams were recovered and the hydrochloride gave  $l=4$ ,  $c=12.3$ ,  $\alpha_D - 1.93^\circ$ ,  $[\alpha]_D - 3.9^\circ$ .

A good growth of *A. gr.* with little sporing almost covering the surface of a similar solution was obtained in 6 weeks, and then 4.8 grams of base were recovered, the hydrochloride giving  $l=4$ ,  $c=14.4$ ,  $\alpha_D - 0.55^\circ$ ,  $[\alpha]_D - 1.0^\circ$ .

### *Alkyloxypropionic Acids.*

*$\alpha$ -Ethoxypropionic acid* was prepared by the action of sodium ethoxide upon ethyl  $\alpha$ -bromopropionate (Schreiner, *Annalen*, 1879, 197, 13).

*P. g.*, when grown in 300 c.c. of a 3 per cent. solution of the acid in the form of ammonium salt, showed a fair growth, and after  $2\frac{1}{2}$  months the aqueous solution of sodium salt (25 c.c.), prepared from the product, gave  $\alpha_D - 0.12^\circ$  ( $l=4$ ). The acid recovered from this by acidification and extraction with ether was also slightly laevorotatory.

*A. gr.*, when cultivated on 500 c.c. of a solution containing 6.2 grams of calcium salt, showed a fair growth. After  $3\frac{1}{2}$  months, 3 grams of inactive salt were removed, and the filtrate (12 c.c.) gave  $\alpha_D + 1.15^\circ$  ( $l=2$ ). The acid prepared from this solution was also distinctly dextrorotatory, the total calcium salt recovered weighing 5 grams.

As the active sodium and calcium ethoxypropionates have a specific rotatory power of about  $48^\circ$  in dilute aqueous solutions (Purdie and Irvine, *Trans.*, 1899, 75, 490), those experiments indicate not only that both the *d*- and *l*-forms are attacked, but also that the difference in rate of attack by the moulds is very slight. In fact, under certain conditions, *P. g.* attacks both forms at the same rate, as it was found in two other separate experiments that this mould grew well on the ammonium salt, but that the resulting acid was quite inactive. Similarly, *A. n.* grows with some difficulty on the calcium salt, yielding an inactive product. In this connection, it may also be observed that Pfeffer (*loc. cit.*) likewise obtained an inactive product when *Aspergillus fumigatus* was grown on ammonium racemate.

*$\alpha$ -Propoxypropionic acid* was kindly placed at our disposal by Drs. Purdie and Lander (*Trans.*, 1898, 73, 871).

*P. g.*, when grown on 41 c.c. of a *N*-potassium salt solution diluted to 200 c.c., showed, after  $2\frac{1}{2}$  months, a fair growth with sporing. The



solution, evaporated to 25 c.c., gave  $\alpha_D - 0.20^\circ$  ( $l=4$ ), and the acid isolated from it was also laevorotatory.

### *$\alpha$ -Hydroxybutyric Acid.*

*P. g.* or *A. n.*, when sown on 200 c.c. of a solution containing the ammonium salt obtained from 8.3 grams of the acid, showed a large growth. In the experiment with *P. g.*, the acid obtained by acidification and extracted with ether was converted into zinc salt, an inactive crop of which was removed whilst the filtrate (49 c.c.) gave  $[\alpha]_D - 5.1^\circ$  ( $c=6.087$ ).

From the solution, on which *A. n.* had been grown, 4.8 grams of acid were recovered, and converted into zinc salt, an inactive crop of which was removed, whilst the filtrate (25 c.c.) gave  $[\alpha]_D - 6.0^\circ$  ( $c=8.752$ ).

Under similar conditions, *A. gr.* showed a good growth of mycelium, but little sporing. After 2 months, 7.2 grams acid were recovered. The filtrate (21 c.c.) from the zinc salt, as before, gave  $[\alpha]_D - 1.0^\circ$  ( $c=14.12$ ).

### *$\beta$ -Hydroxybutyric Acid.*

In 2 months a large growth of *P. g.* was obtained in 100 c.c. of a 4 per cent. solution of the acid in the form of its ammonium salt. The product was laevorotatory, and an aqueous solution (12 c.c.) of the acid obtained from it, by acidification and extraction with ether, gave  $\alpha_D - 0.22^\circ$  ( $l=2$ ); 3.0 grams acid were recovered.

*A. n.*, cultivated on a solution of the ammonium salt (3.5 grams of acid in 100 c.c.), showed in  $2\frac{1}{2}$  months an abundant mycelium growth with incipient sporing. An aqueous solution (12 c.c.) of the acid gave  $\alpha_D - 0.06^\circ$  ( $l=2$ ), 2 grams of acid being recovered.

*A. gr.*, when cultivated on a solution of ammonium salt containing 3 grams of acid in 1000 c.c., grew well in 1 month. An aqueous solution of the acid gave  $\alpha_D + 0.33^\circ$  ( $l=4$ ) and  $[\alpha]_D + 2.7^\circ$ . 0.8 gram of acid was recovered.

As  $[\alpha]_D$  of the active  $\beta$ -hydroxybutyric acids is equal to  $24.8^\circ$  (McKenzie, Trans., 1902, 82, 1404), the *d*-form appears to be attacked by *P. g.* and *A. n.* more readily than the *l*-form, but less readily by *A. gr.* Although the *d*-form is a better medium for the growth of *P. g.* than the *l*-form, the mould flourishes exceedingly well in a suitable solution of the latter, as shown by the following experiment.

*P. g.*, when grown on a solution (100 c.c.) containing 1.1 grams of *l*-acid in the form of ammonium salt, grew well, the surface being quite covered by mycelium and spores. After 1 month, 0.7 gram of *l*-acid was recovered.

*Glyceric Acid.*

It was noted by Lewkowitsch (*Ber.*, 1883, 16, 2720) that, when *P. g.* was grown on ammonium glycerate, the solution became lævoro-rotatory. *Bacillus ethaceticus* has been used by Frankland and his pupils for the preparation of *d*-glyceric acid and its derivatives (*Trans.*, 1891, 59, 81, &c.).

In  $2\frac{1}{2}$  months, a large mycelium growth of *P. g.* with abundant sporing was obtained on a solution containing 8 grams of calcium glycerate in 200 c.c.; 4.5 grams of salt were removed, which, when dissolved in dilute hydrochloric acid, gave (25 c.c.)  $a_D + 0.11^\circ$  ( $l = 4$ ). The filtrate (32 c.c.) gave  $[\alpha]_D - 5.9^\circ$  ( $c = 4.26$ ), and, when acidified, became dextrorotatory in accordance with Frankland's observations. The total salt recovered was 6 grams.

A comparable experiment with *A. n.* gave similar results. After 3 weeks, 6 grams of salt were withdrawn, whilst the filtrate (25 c.c.) gave  $a_D - 0.39^\circ$  ( $l = 4$ ).

*A. gr.* was cultivated under similar conditions, and, after  $2\frac{1}{2}$  months, 5.2 grams of salt were withdrawn. The filtrate (36 c.c.) gave  $[\alpha]_D - 5.2^\circ$  ( $c = 4.39$ ), and, when acidified, became dextrorotatory. The total salt recovered = 7 grams.

Hydrated calcium glycerate has  $[\alpha]_D^{17} - 11.66^\circ$  ( $c = 10$ ) (Frankland and Appleyard, *Trans.*, 1893, 63, 296).

*Malic Acid.*

Malic acid was prepared from monobromosuccinic acid by silver oxide according to Kekulé's process. *P. g.* Calcium salt from 2 grams of acid; 600 c.c.; good growth with little sporing; 1 month. The rotations of the product and of the acid obtained from it were so slight that they could not be directly observed. This was to be expected from the low values which *l*-malic acid and its calcium salt are known to possess. The rotation of the malic acid in the above solution was rendered obvious, however, by Walden's uranyl nitrate reagent (*Ber.*, 1897, 30, 2889) by the use of which a marked lævoro-rotation was noted.

*Alkylloxysuccinic Acids.*

For specimens of those acids we are indebted to Dr. Purdie. Under the conditions employed by us, the various moulds either did not grow at all or the growth was, as a rule, feeble, as in the two following instances.

*Methoxysuccinic Acid.*—*P. g.* Two grams of ammonium hydrogen

salt; 200 c.c.; slight mycelium growth with little sporing; an inactive crop was separated, and the filtrate (25 c.c.) gave  $\alpha_D -0.09^\circ$  ( $l=4$ ).

*Propoxysuccinic Acid*.—A slight growth of *P. g.* took place with the calcium salt but the product was inactive.

*Ethoxysuccinic Acid*.—In this case a fair growth of *P. g.* was obtained on the calcium salt solution but no activity was observed with the product.

With the potassium salt from 43.1 c.c. of *N*-acid solution diluted to 1000 c.c., a good growth of *P. g.* was obtained. After 2 months, the acid was extracted with ether, 32.5 c.c. of *N*-acid solution being recovered. This gave  $\alpha_D -0.37^\circ$ ,  $l=4$ ,  $c=9.8$ , hence  $[\alpha]_D -0.9^\circ$ .

#### *Mandelic Acid.*

*P. g.*; 15 grams of acid, to which 9/10 of the calculated amount of potassium hydroxide solution was added; 500 c.c.; the growth was slight. After 4 months, the solution was filtered, neutralised, re-sterilised, and resown. After 6 weeks, the growth was again slight. By acidification and extraction with ether, 14 grams of acid were recovered, a saturated aqueous solution of which appeared to be inactive. The activity was rendered apparent by the following method. After 4.5 grams of the *r*-acid had crystallised out, the filtrate was converted into barium salt, a crop of the *r*-salt separated, and the filtrate, when made up to 25 c.c., gave  $\alpha_D -0.12^\circ$  ( $l=4$ ).

In another experiment, 13.5 grams were converted into ammonium salt and made up to 500 c.c.; the growth again was slight; after 4 months, 10 grams of acid, a 10 per cent. aqueous solution of which was feebly laevorotatory, were recovered. The direction of rotation was confirmed as indicated in the previous experiment.

When 3 grams of acid were converted into ammonium salt and made up to 1000 c.c., the growth was again slight. After 4 months the resulting solution was concentrated and when exactly neutralised by ammonia gave  $\alpha_D -0.11^\circ$  ( $l=4$ ) for 25 c.c.

The above results differ altogether from those of Lewkowitsch (*Ber.*, 1882, 15, 1506; 1883, 16, 1568), who states that *P. g.* grows well in a solution of ammonium mandelate, and that, after one crystallisation of the resulting acid, the pure *d*-mandelic acid may be obtained. On the contrary, in our experience the growth of a pure culture of the mould in question takes place with difficulty and the product is faintly, but distinctly, laevorotatory. In addition to the experiments quoted, six others were performed with solutions of the strength employed by Lewkowitsch, and the results were similar in every case. We find, however, that a considerable resolution may be attained by certain bacteria, for example, a solution of ammonium



mandelate with the usual inorganic food material was purposely allowed to become spontaneously infected by bacteria from the air, when a vigorous growth occurred yielding a *dextrorotatory* acid with  $[\alpha]_D + 33^\circ$ . In one experiment described by Lewkowitsch where he obtained a mycelium growth under the surface of the liquid, the resulting acid was *laevorotatory*, 0.1 grams of *l*-acid being calculated as produced from 3 grams of the inactive substance. The direction of rotation accords, in this case, with our results. From observations made by Pfeffer (*loc. cit.*) and from our experiments, we conclude that the resolution of mandelic acid attained by Lewkowitsch was not effected by *P. g.*

One other observation made by Lewkowitsch is contradictory. He found that acidified solutions containing *d*-mandelic acid, when left exposed to air, became covered by moulds by spontaneous infection, whilst acidified solutions containing the *l*-acid did not. Spores of *P. g.* introduced into the latter did not grow.

*A. n.* and *A. gr.* differ from one another in giving *laevo*- and *dextro*-rotatory products respectively.

*A. n.*—6.75 grams of acid in 250 c.c. were converted into ammonium salt, to which 0.75 grams acid were then added. Considerable mycelium growth at bottom of flask; slight growth on surface with little sporing. After 4 months, 5.8 grams of acid were recovered:  $l=4$ ,  $c=11.6$ ,  $\alpha_D - 1.46^\circ$ ,  $[\alpha]_D - 3.1^\circ$ .

*A. gr.* showed a marked growth when cultivated on a solution (500 c.c.) of 15 grams of acid neutralised by the calculated amount of potassium hydroxide. After 3 months, 13.5 grams of acid were recovered:  $c=13.5$ ,  $\alpha_D + 0.17^\circ$  ( $l=4$ ).

*A. gr.* grew well on a 500 c.c. solution of 3 grams of acid neutralised by ammonia. After 4 months, 2.1 grams of acid were recovered:  $l=4$ ,  $c=7.144$ ,  $\alpha_D + 8.33^\circ$ ,  $[\alpha]_D + 29.2^\circ$ .

### *Alkylxyphenylacetic Acids.*

*Methoxyphenylacetic acid* was prepared by alkylating mandelic acid with silver oxide and methyl iodide (McKenzie, Trans, 1899, 75, 753).

*P. g.*, when cultivated on 500 c.c. of a 1 per cent. solution of the sodium salt, grew only slightly. After 4 months, a crop of the inactive sodium salt was separated; the filtrate (12 c.c.) gave  $\alpha_D - 0.13^\circ$  ( $l=2$ ) and the acid obtained from it was also *laevorotatory*.

The *laevorotation* was confirmed by an experiment with the ammonium salt. In both cases the salts were attacked by the mould only to a slight extent. *A. n.* and *A. gr.* gave very feeble growths in solutions of the sodium and ammonium salts, and no definitely active products were isolated.

*Ethoxyphenylacetic acid* was prepared by the action of sodium ethoxide upon ethyl chlorophenylacetate. Under the conditions employed, it was found impossible to obtain satisfactory growths of the various moulds. *P. g.* and *A. gr.* appeared to give slightly lævorotatory and dextrorotatory products respectively.

*Propoxyphenylacetic acid* was prepared by alkylating mandelic acid with silver oxide and propyl iodide.

*P. g.*, when cultivated on 100 c.c. of a solution containing the ammonium salt from 3.9 grams acid, gave a fair mycelium growth without sporing. After 2 months the acid (2.2 grams) was converted into calcium salt. One gram *r*-salt was removed, and the filtrate acidified and extracted with ether. The resulting acid was converted into sodium salt, the aqueous solution of which (25 c.c.) gave  $\alpha_D - 0.20^\circ$  ( $l = 4$ ).

*A. n.*, when grown on a solution of equal strength, gave only a slight mycelium growth with some sporing. After 4 months, the ethereal solution (42 c.c.) of the acid obtained was lævorotatory, 25 c.c. of it giving  $\alpha_D - 0.27^\circ$  ( $l = 4$ ). The barium salt prepared from this was also lævorotatory. The total acid recovered = 3.4 grams.

In the action of pure cultures of *P. g.*, *A. n.* and *A. gr.* on salts of inactive acids, our experience in most cases tends to show that the mode of action is such that the mould attacks the one active isomeride more readily than the other, and that the extent of the resolution depends solely upon the difference of the rate of attack. For obtaining the pure active isomeride, the method is unsuitable. In several cases a good growth of the mould can be induced and yet either no resolution at all or a very slight one results; the inference here is that the rates of attack of the mould on the two active forms is either equal or approximately so. Again, the substitution of the hydroxyl groups of aliphatic hydroxy-acids by alkyloxy-groups has a very marked effect on the growth of the various moulds, which cannot be purely accidental. Whilst the moulds flourished exceedingly well in the solutions of tartrates, lactates, and malates examined, they grew badly in solutions of dimethoxysuccinates, alkyloxypropionates and alkyloxysuccinates respectively, many unsuccessful attempts having been made to obtain suitable solutions of the latter substances before the organisms could be induced to multiply in them at all. Those phenomena are not to be accounted for on stereochemical grounds, as the experimental evidence submitted by Purdie and others shows that the configuration of the alkyloxy-acid corresponds with that of its related hydroxy-acid. On the other hand, the fact that *P. g.* and *A. n.* grow well in ammonium fumarate but practically not at all in ammonium maleate (E. Buchner, *Ber.*, 1892, 25, 1161) may possibly be partly attributed to spatial influence, and within the same category may also be classified the results of Emmerling, who finds that various related amino-

acids differ in a marked degree from one another, when regarded as sources of food material for moulds. For example, those moulds which grow excellently on  $\alpha$ -amino- $\beta$ -hydroxypropionic acid, do not grow at all on the isomeric  $\beta$ -amino- $\alpha$ -hydroxypropionic acid (*Ber.*, 1902, 35, 2290).

In the following list the rotation of the product after growth of the mould is quoted :

| Acid.                      | <i>P. g.</i> | <i>A. n.</i> | <i>A. gr.</i> | Acid.               | <i>P. g.</i> | <i>A. n.</i> | <i>A. gr.</i> |
|----------------------------|--------------|--------------|---------------|---------------------|--------------|--------------|---------------|
| Racemic .....              | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Methoxysuccinic...  | <i>l</i> -   | —            | —             |
| Dimethoxysuccinic          | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Ethoxysuccinic ...  | <i>l</i> -   | —            | —             |
| Lactic .....               | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Propoxysuccinic ... | <i>l</i> -   | —            | —             |
| $\alpha$ -Aminopropionic.. | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Mandelic .....      | <i>l</i> -   | <i>l</i> -   | <i>d</i> -    |
| $\alpha$ -Ethoxypropionic. | <i>l</i> -   | <i>i</i> -   | <i>d</i> -    | Methoxyphenyl-      |              |              |               |
| $\alpha$ -Propoxypropionic | <i>l</i> -   | —            | —             | acetic.....         | <i>l</i> -   | —            | —             |
| $\alpha$ -Hydroxybutyric.  | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Ethoxyphenyl-       |              |              |               |
| $\beta$ -Hydroxybutyric.   | <i>l</i> -   | <i>l</i> -   | <i>d</i> -    | acetic.....         | <i>l</i> -   | —            | <i>d</i> -    |
| Glyceric .....             | <i>l</i> -   | <i>l</i> -   | <i>l</i> -    | Propoxyphenyl-      |              |              |               |
| Malic.....                 | <i>l</i> -   | —            | —             | acetic.....         | <i>l</i> -   | <i>l</i> -   | —             |

The regularity with which a *laevorotatory* product was formed by *P. g.* and *A. n.* is striking, especially if we consider other resolutions described by previous investigators, for instance, the following compounds gave, with *P. g.*, *laevorotatory* products in every case: leucine (Schulze and Likiernik, *Ber.*, 1891, 24, 671); glutaminic acid (Schulze and Bosshard, *Zeit. physiol. Chem.*, 1886, 10, 143); mannonic acid lactone (E. Fischer, *Ber.*, 1890, 23, 379); phenyl-glycidic acid (Plöchl and Meyer, *Ber.*, 1897, 30, 1611).

Under symmetrical conditions it is impossible that a *d*-stereoisomeride can undergo chemical transformation at a different rate from the *l*-form. The assumption may accordingly be hazarded that, during the type of resolution described in this paper, two distinct compounds, which are not mirror-images, are formed during the mould-growth by combination of each of the active isomerides with one and the same optically active asymmetric complex; the rate of formation could, on theoretical grounds, be different, and the two hypothetical compounds could also undergo chemical change at different rates (compare Marckwald and McKenzie, *Ber.*, 1899, 32, 2130, &c.). We were led, accordingly, to attempt to show the presence of an optically active enzyme produced by growth of *P. g.*, and, further, to see whether it was possible to resolve an inactive acid by enzyme action without an actual mycelium growth and sporing of the mould in the solution under experiment. The following experiment, although far from being convincing, may be quoted.



A large growth of *P. g.* was obtained on a suitable medium, the mycelium and spores were separated and ground up with 'kieselguhr' by the aid of Rowland's apparatus (*J. Physiol.*, 1901, 27, 53), and, when the cells had been disintegrated, the juice was extracted by application of the requisite pressure. This extract was slightly dextrorotatory, and microscopic examination failed to show the presence of any spores. It was introduced into 50 c.c. of a sterile, aqueous *N*-potassium lactate solution (containing a little toluene), and a current of sterilised oxygen was passed through continuously for 14 days, during which time carbonic acid gas was being slowly evolved. The solution was then quite clear, and was perfectly free from mycelium or spores of *P. g.* and also from bacteria. The lactic acid, prepared from it, was converted into zinc salt, 5 grams of which were withdrawn; the filtrate measured 35 c.c., 25 c.c. of which gave  $\alpha_D - 0.08^\circ$  ( $l = 4$ ).

It has been pointed out by E. Fischer (*Ber.*, 1894, 27, 2992) that those modifications of different bodies, which are attacked by the same enzyme, must possess analogous configurations. Whilst there is no definite proof that the resolution of an inactive substance by a mould is to be ascribed to enzyme action, our results may be interpreted in the light of what has been experimentally shown as to the relationship in configuration between the various related acids examined.\*

The configuration of *d*-tartaric, *d*-malic, *d*-alkyloxysuccinic and *d*-dimethoxysuccinic acids is identical; there is, for instance, no inversion when *d*-tartaric acid is converted into *d*-dimethoxysuccinic acid. In accordance with this, it might be expected that, when a mould resolves racemic acid, giving a levorotatory product, the same mould would resolve the other acids mentioned to give a product of the same sign of rotation; this was the case in our experiments. It should be mentioned, however, that Purdie and Walker obtained *d*-ethoxysuccinic acid by growing *P. g.* on ammonium hydrogen ethoxysuccinate (*Trans.*, 1893, 63, 230), but as we have obtained a contrary result, we are inclined to think that their resolution was accomplished by the agency of some organism different from that used by us. There is, again, no inversion when active lactic acid is converted into the active alkyl-oxypropionic acids, and accordingly *P. g.*, for example, resolves those corresponding inactive acids to give a preponderance of the *l*-forms.

\* Bremer (*Ber.*, 1875, 8, 1594); E. Fischer (*Ber.*, 1896, 29, 1377); Winther (*Ber.*, 1895, 28, 3000); E. Fischer and Thierfelder (*Ber.*, 1894, 27, 2036); E. Fischer (*Ber.*, 1894, 27, 2985, 2992, 3479; 1895, 28, 1429; *Zeit. physiol. Chem.*, 1898, 26, 60); Walden (*Ber.*, 1896, 29, 133; 1897, 30, 2795, 3146; 1899, 32, 1833, 1855); Purdie and Walker (*Trans.*, 1893, 63, 242); Purdie and Williamson (*Trans.*, 1895, 67, 932); Purdie and Lander (*Trans.*, 1898, 73, 301, 874); Purdie and Irvine (*Trans.*, 1899, 75, 483; 1901, 79, 957); Purdie and Barbour (*Trans.*, 1901, 79, 972).

It is also likely that the configuration of mandelic acid and the alkyloxyphenylacetic acids derived from it is the same, as *P. g.* gave *l*-products in the cases examined. The results with alanine are also such as might be expected from the considerations just expressed. The dextrorotatory ethoxypropionic acid formed by *A. gr.* presents an exception.

Now Walden has shown that, when the esters of *l*-malic acid are converted into the halogen-succinic esters by phosphorus halide, there is a change in the sign of rotation but none in the configuration, and he indicates this latter point by designating as *l*-halogen-succinic esters the dextrorotatory esters derived from *l*-malic esters (*Ber.*, 1899, 32, 1859). By the "normal" action of sodium hydroxide, the original *l*-malic acid may be regenerated from *l*-halogen-succinic acid without any change of configuration; inversion takes place, however, during the "abnormal" action of silver oxide. On those grounds, we supposed that when *P. g.* was grown on solutions of the halogen derivatives of the hydroxy-acids examined, the products of the growths should be *dextrorotatory*. We accordingly grew the various moulds on solutions of salts of  $\alpha$ -bromopropionic,  $\alpha$ -bromobutyric, and chlorophenylacetic acids, but the amount of conversion into the salts of the corresponding lactic,  $\alpha$ -hydroxybutyric, and mandelic acids by the action of water was so great as to render the detection of a dextrorotatory product difficult. On the other hand, with monobromosuccinic acid there was distinct evidence that a dextrorotatory acid was formed by the action of *P. g.* Monobromosuccinic acid (16 grams) was neutralised by ammonia, and the solution (400 c.c.) was sterilised as usual and sown with *P. g.* The growth of the mould was fairly rapid and extensive. On evaporation of the solution and extraction with ether (in which malic acid is hardly soluble), bromosuccinic acid was obtained, and 25 c.c. of its aqueous solution (110 c.c.) gave  $\alpha_D +0.15^\circ$  ( $l=4$ ). It was found possible to convert this acid into the corresponding levorotatory calcium malate. A similar result was obtained in a second experiment which need not be quoted. In those experiments, it must be remembered that we were actually dealing with the action of *P. g.* on a mixture of bromosuccinate and malate, since during the sterilisation of the original solution a considerable portion of the bromosuccinate was inevitably converted into malate by the action of water (compare Müller, *Zeit physikal. Chem.*, 1902, 41, 483). When the mould grew in this mixture, it attacked the bromosuccinate and the malate to give dextrorotatory and levorotatory products respectively. When *A. n.* was grown on a mixture of the calcium salts of monobromosuccinic and malic acids, a dextrorotatory bromosuccinic acid was also obtained along with a levorotatory malic acid, the direction of the rotation of





leaving the question of the isomerism between pilocarpine and isopilocarpine an open one.

Although the experimental results recorded in this paper show that the above formula is possibly correct, yet the evidence from which Pinner and Schwarz deduced their formula is open to criticism.

Whilst these authors have confirmed my statements regarding the formation of homopilopie acid by the oxidation of isopilocarpine, they have not proved that this acid is produced when pilocarpine is oxidised. The diamide of the acid obtained by them from pilocarpine by oxidation melted at  $182^{\circ}$ , whilst the diamide of homopilopie acid melts at  $208^{\circ}$ . Therefore either the acid produced by the oxidation of pilocarpine is isomeric and not identical with homopilopie acid, or the diamide obtained by Pinner and Schwarz was impure. The experiments recorded in this paper show that the latter is the correct explanation, and that when pilocarpine is oxidised, homopilopie acid, identical in all respects with that previously described, is produced. Pinner and Schwarz have also stated that certain conclusions made by me with regard to the existence of the :NH group in isopilocarpine are incorrect,\* and offer another explanation of the facts. I have proved that their explanation is correct by preparing directly from isopilocarpine methiodide the picrate previously supposed to be methyl isopilocarpine picrate. The compound thus previously described should therefore be named isopilocarpine methyl picrate.

In former papers I showed that isopilocarpine and pilocarpine contain no ordinary double bond, and further experiments recorded in this paper demonstrate the extraordinary stability of isopilocarpine towards reducing agents, and also prove its mono-acidic character, which had previously been shown to be due to the nitrogen atom other than the methylamine residue.

Pinner and Schwarz seem to have overlooked these facts, as they describe (*Ber.*, 1902, 35, 204, 2443) similar experiments to prove that bromine forms substitution and not additive compounds, and make no mention of my results. Moreover, I gave the most conclusive proof of the composition of the dibromo-compounds by reducing them to the original alkaloids (*Trans.*, 1901, 79, 601). It is unfortunate that Pinner and Schwarz were not able to adduce more conclusive proof of the formation of methylurea by the oxidation of pilocarpine. If, however, a small amount of this base were formed it would not necessitate the existence of a glyoxaline ring in the pilocarpine molecule, as it might be equally well produced from the betaine formula mentioned in the latter part of the paper. It is true that Pinner and Schwarz have shown that there is an analogy between certain reactions

\* I had arrived at this opinion before the publication of Pinner and Schwarz's paper, but was reserving the correction until the results could be fully discussed.

of pilocarpine and its derivatives and those of glyoxaline, yet, as is shown in the latter part of this paper, there are several other formulae equally probable, including the isomerides dependent on the point of attachment of the non-nitrogenous group to the nitrogen ring. In consideration of all these points, and in view of the experimental results recorded in this and the following paper (p. 464), I am able to confirm with a certain reservation the formula for pilocarpine suggested by Pinner and Schwarz.

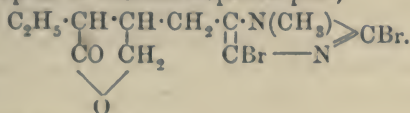
The constitution of homopolipic acid having been determined, the problem of the nature of the remainder of the molecule has been attacked from two points. Firstly, by preparing substances containing possibly the same group as *isopilcarpine*, and studying their behaviour with certain reagents in order to determine if there was any analogy between them and this alkaloid. The substances thus studied were 1:4(or 1:5)-dimethylglyoxaline and 1:3-dimethylpyrazole, and the results are recorded in the following paper. Secondly, by endeavouring to obtain from *isopilcarpine* substances containing the nitrogen ring intact, which has been accomplished by distillation with soda lime. From the crude product thus obtained 1-methylglyoxaline, 1:4(or 1:5)-dimethylglyoxaline, 1:4(or 1:5)-methylamylglyoxaline, and probably 1:4(or 1:5)-methylamyleneglyoxaline have been isolated and identified. The identification of the first three substances has been rendered conclusive by the preparation and analysis of crystalline derivatives and by their products of oxidation. It may be mentioned that the aurichloride of the substance described in an early paper (Trans., 1900, 17, 853) as methylpyridine was undoubtedly dimethylglyoxaline. The analytical figures agree equally well for the latter substance, and a small amount of impurity would account for the low melting point. The bearing of these and previous results on the constitution of *isopilcarpine* is fully discussed, and the following formula proposed for *isopilcarpine*. It will be seen that I is identical with that suggested by Pinner and Schwarz,

The difficulty in deciding between these two formulæ is due to the fact that the constitution of the 4(or 5)-methylglyoxaline of Gabriel and Pinkus (*Ber.*, 1893, 26, 2205) cannot be stated with certainty. The determination of the constitution of the latter will conclusively decide between formulæ I and II.

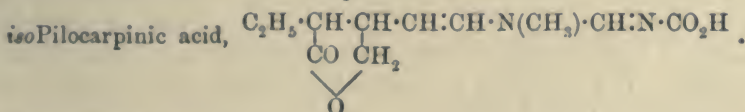
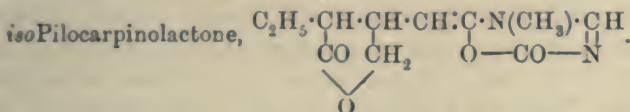
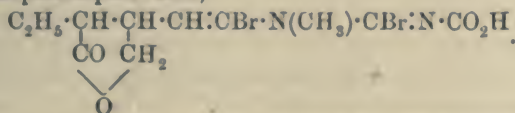
The relationship of pilocarpine to *isopilocarpine* is considered, and the conclusion arrived at is that they are stereoisomerides, the asymmetric carbon atom involved being that contiguous to the carboxyl residue. This conclusion is strongly supported by the fact that the absorption spectra of the two alkaloids are absolutely identical.

The formulæ for the following substances are suggested after consideration of their reactions; they are based on formula I for *isopilocarpine*, and if II should prove correct will require slight modification.

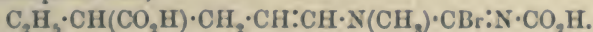
Dibromopilocarpine or dibromo*isopilocarpine*,



Dibromo*isopilocarpinic* acid,



Bromocarpinic acid,



It is shown that the explanation given by Pinner and Schwarz of the formation of pilocarpoic acid,  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{N}_2$ , is quite untenable, and no suggestions as to the constitution of this, or pilomalic acid, are offered.

It seems desirable at this stage of the inquiry to state briefly some of the results obtained, concerning which there has been some uncertainty, in order to prevent confusion in chemical literature. From the products of the oxidation of pilocarpine or *isopilocarpine* with permanganate, besides ammonia and methylamine, and small amounts of acetic and propionic acids, pilopic and homopilopic acids—lactonic acids of the formula  $\text{C}_7\text{H}_{10}\text{O}_4$  and  $\text{C}_8\text{H}_{12}\text{O}_4$ —have been isolated in amounts



varying with the conditions of experiment. These substances occur in the oxidation liquors as the potassium salts of the corresponding hydroxy-acids. These acids may be considered to be the lactonic acids of  $\alpha$ -hydroxymethyl- $\beta$ -ethylsuccinic and  $\beta$ -hydroxymethyl- $\alpha$ -ethylglutaric acids, though complete proof of this can only be obtained by synthesis. The acid obtained by Pinner and Kohlhammer by the oxidation of pilocarpine, which was first named by them *piluvic acid*,  $C_8H_{12}O_5$ , and subsequently *homopilomalic acid*,  $C_8H_{14}O_5$ , was undoubtedly homopilopic acid, though the salts examined by them were those of the corresponding hydroxydibasic acid. As this hydroxy-acid is unstable, immediately losing water with formation of the lactonic acid, and as Pinner and Schwarz in their last paper definitely accept my conclusions regarding this acid, the names *piluvic* and *homopilomalic acid* may be abandoned. The acid,  $C_7H_{12}O_5$ , obtained by Pinner and Kohlhammer by the oxidation of pilocarpoic acid, which was first named *isohydrochelidonic acid* and subsequently *pilomalic acid*, appears to be a distinct acid, and not the hydroxy-acid of pilopic acid; it should therefore be considered as an acid of unknown constitution.

With regard to Pinner and Schwarz's suggestion to alter the name of the acid, first described by me, from *dibromoisopilocarpinic* to *dibromoisocarpoic acid* on account of its possible confusion with *dibromoisopilocarpic acid*, I see no reason for such a change, and would prefer to retain the original name for this acid. The confusion has arisen by an incorrect translation of these names into German, the acid obtained from *dibromoisopilocarpine* and corresponding to the acid of which *isopilocarpine* is the lactone is *dibromoisopilocarpic acid* or "*dibromoisopilocarpinsäure*," whereas *dibromoisopilocarpinic acid* would be "*dibromoisopilocarpininsäure*," and not "*dibromoisopilocarpinsäure*" as rendered by Pinner and Schwarz (compare also *Chem. Centr.*, 1901, i, 1059). The difference in terminology would thus be the same in German as in English, and no new name is required.

Finally, in view of the researches which have resulted in establishing the constitution of pilocarpine (compare Feist, *Arch. Pharm.*, 1902, 240, 3), it would seem important that the widely quoted statements of Hardy and Calmels regarding this alkaloid, including its alleged synthesis by them, should now cease to receive scientific recognition.

#### EXPERIMENTAL.

##### *Distillation of isoPilocarpine with Soda-lime.*

After several preliminary experiments, the best method of procedure was found to be as follows. One part of *isopilocarpine* nitrate was mixed with eight times its weight of a mixture of equal parts of soda-lime and slaked lime and the mixture then placed in an iron tube,

which fitted into an ordinary combustion furnace, replacing the bed on which the glass combustion tube usually rests. The tube was closed at each end by caps, which could be unscrewed, and contained iron delivery tubes at each end. It was filled so that a clear space was left above the powder, the air displaced with hydrogen, the tube then gradually heated, and the gases, &c., evolved passed into aqueous hydrochloric acid. When the whole length of tube had been heated and no more gas was evolved, hydrogen was passed through. The acid solution was then boiled with a little animal charcoal, filtered, and extracted with ether; the acid liquid was then made decidedly alkaline with excess of caustic alkali, extracted several times with ether, the ethereal solution washed with water, dried over potassium carbonate and distilled.

The residue, which was a dark-coloured, strongly smelling liquid, was next distilled under diminished pressure, and the portion distilling between  $100^{\circ}$  and  $200^{\circ}$  under 10 mm. pressure collected. The yield of distillate was about 17 per cent. of the base taken. It was then distilled several times under 10 mm. pressure and the following fractions collected:

(1) B. p.  $100-120^{\circ}$ , 1 part. (2) B. p.  $120-150^{\circ}$ , 1 part. (3) B. p.  $150-160^{\circ}$ , 5 parts.

These fractions were then further examined.

*Fraction b. p.  $100-120^{\circ}$  under 10 mm. Pressure.*

This was a colourless liquid with the characteristic odour of a glyoxaline, rapidly becoming brown, and immiscible with water. An attempt to distil it under the ordinary pressure was not very successful, and though the chief portion boiled at  $210-215^{\circ}$ , decomposition occurred, and a large proportion of the whole was left behind in the flask as a thick, red oil.

The distillate was analysed:

0.1406 gave 0.3418  $\text{CO}_2$  and 0.108  $\text{H}_2\text{O}$ . C = 66.3; H = 8.5.

$\text{C}_5\text{H}_8\text{N}_2$  requires C = 62.5; H = 8.3 per cent.

The analytical figures and its behaviour towards various reagents (*vide infra*) showed that this fraction, despite its fairly constant boiling point, was far from pure.

*Fraction b. p.  $120-150^{\circ}$  under 10 mm. Pressure.*

This fraction, which was very small for such a wide range of temperature, was so evidently a mixture that it was not further examined. It

became oxidised and discoloured much more rapidly than either of the other fractions.

*Fraction b. p. 150—160° under 10 mm. Pressure.*

This was by far the largest fraction, and was a thick, yellow liquid which slowly became discoloured, but was much more stable than either of the other fractions. A portion, which boiled at 158—160° under 10 mm. pressure, was analysed with the following result :

0.213 gave 0.5610 CO<sub>2</sub> and 0.176 H<sub>2</sub>O. C = 71.8 ; H = 9.2.

0.1956 „ 0.5148 CO<sub>2</sub> „ 0.160 H<sub>2</sub>O. C = 71.8 ; H = 9.1.

0.075 „ 12.8 c.c. nitrogen at 17° and 745 mm. N = 19.0.

C<sub>9</sub>H<sub>14</sub>N<sub>2</sub> requires C = 72.0 ; H = 9.3 ; N = 18.7 per cent.

C<sub>9</sub>H<sub>16</sub>N<sub>2</sub> „ C = 71.1 ; H = 10.5 ; N = 18.4 „

Although the analytical figures agree remarkably well for those required for the formula C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>, an amount of impurity might be present, as in the first fraction, to cause the slight variation from the numbers required for the formula C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>. Other experiments, shortly to be described, show that the fraction contained substances corresponding to both of the above formulæ.

*Identification of 1-Methylglyoxaline.*

In view of the fact that the lowest members of the glyoxaline series are not readily extracted from their aqueous solution by ether, the alkaline liquid after extraction with ether (p. 465) was neutralised, evaporated to a low bulk, and treated by the method described for the isolation of methylglyoxaline. The ethereal solution left, after removal of the ether by distillation, a liquid which distilled completely at 200—205°. This colourless liquid had the peculiar odour characteristic of the glyoxalines, was miscible with water, alcohol, or ether, and was quite stable :

0.1882 gave 0.4146 CO<sub>2</sub> and 0.134 H<sub>2</sub>O. C = 60.1 ; H = 7.9.

C<sub>4</sub>H<sub>6</sub>N<sub>2</sub> requires C = 58.5 ; H = 7.3 per cent.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub> „ C = 62.5 ; H = 8.3 „

The analytical figures indicating a mixture of methyl- and dimethylglyoxalines, the picrate and platinichloride were prepared and examined.

*Platinichlorides.*—These were prepared by fractional precipitation with platinic chloride.

The first fraction melted at 239° and on analysis :

0.1028 gave 0.0334 Pt. Pt = 32.5.

(C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 32.4 per cent.



The fifth fraction melted at  $195^{\circ}$  and on analysis:

0.0678 gave 0.0228 Pt. Pt = 33.6.

$(C_4H_6N_2)_2, H_2PtCl_6$  requires Pt = 33.9 per cent.

The intermediate fractions melted between  $195^{\circ}$  and  $239^{\circ}$ .

The *picrates* were prepared by precipitating a solution of the hydrochloride with picric acid. The crystalline precipitate melted at  $157^{\circ}$ , but after frequent recrystallisation two fractions were obtained melting at  $158^{\circ}$  and  $167^{\circ}$  respectively, and further crystallisation did not affect these melting points; 1-methylglyoxaline boils at  $197-199^{\circ}$ , its platinichloride melts at  $190-191^{\circ}$ , and its picrate at  $158^{\circ}$  (*Ber.*, 1889, 22, 1359).

The constants of dimethylglyoxaline and its salts agree with these recorded in the next section of the paper.

The fraction b. p.  $200-205^{\circ}$  contained, therefore, 1-methylglyoxaline and dimethylglyoxaline.

#### *Identification of 1:4(or 1:5)-Dimethylglyoxaline.*

The hydrochloride of the fraction boiling at  $100-120^{\circ}$  under 10 mm. pressure, does not crystallise, and the platinichloride and aurichloride, when prepared in the usual way, undergo reduction, but the former double salt was obtained as follows. The oil was shaken up with three times its volume of water and the aqueous layer separated and converted into the hydrochloride. On adding platinic chloride a yellow crystalline precipitate was obtained which was separated and examined. When prepared in this way the platinichloride had no tendency to undergo reduction.

*Dimethylglyoxaline platinichloride*, when crystallised from hot water, separated in orange-coloured, cubical crystals, which melted at  $238-239^{\circ}$  with decomposition. The melting point was not affected by further recrystallisation. When mixed with an equal weight of 1:4(or 1:5)-dimethylglyoxaline platinichloride (see following paper) the mixture melted at  $238-239^{\circ}$ :

0.0678 gave 0.0222 Pt. Pt = 32.7.

0.104 „ 0.0336 Pt. Pt = 32.3.

0.1174 „ 0.0380 Pt, 0.087  $CO_2$ , and 0.039  $H_2O$ . Pt = 32.4;  
C = 20.2; H = 3.7.

0.112 gave 8.8 c.c. nitrogen at  $17^{\circ}$  and 745 mm. N = 8.9.

$(C_5H_8N_2)_2, H_2PtCl_6$  requires Pt = 32.4; C = 20.0; H = 3.0; N = 9.3 per cent.

*Dimethylglyoxaline aurichloride* was prepared from the hydrochloride obtained by decomposing the platinichloride with hydrogen sulphide. On adding auric chloride to the aqueous solution of the hydrochloride,

yellow acicular crystals separated, which, when collected and dried, first on a porous tile, and then in a desiccator over sulphuric acid, melted at 214—215°:

0.1096 gave 0.0492 Au, 0.0566 CO<sub>2</sub>, and 0.0252 H<sub>2</sub>O. Au = 44.9;  
C = 14.1; H = 2.5.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>,HAuCl<sub>4</sub> requires Au = 45.1; C = 13.8; H = 2.1 per cent.

The pure hydrochloride in 2 per cent. aqueous solution was optically inactive.

*Dimethylglyoxaline picrate*, prepared from the pure hydrochloride by precipitation with picric acid, formed yellow acicular crystals which melted at 167°. The melting point was not affected by further recrystallisation from water or alcohol. When mixed with an equal weight of 1:4(or 1:5)-dimethylglyoxaline picrate (m. p. 167°), the mixture melted at 140—145°. This experiment was repeated several times with different specimens with confirmatory results.

*Oxidation of the fraction boiling at 100—120° with potassium permanganate*.—In order to obtain further proof of the presence of dimethylglyoxaline in this fraction, the whole liquid containing the portions both soluble and insoluble in water was oxidised with permanganate and the products of oxidation isolated and examined.

Three grams of oil required 15 grams of permanganate in 1 per cent. aqueous solution to produce a permanent colour, and the resulting liquid after removing the manganese peroxide by filtration was worked up in the usual manner.

The bases obtained were identified as ammonia and methylamine. The platinum salt of the latter base was analysed.

0.1758 gave 0.0732 Pt. Found Pt = 41.6. Calculated Pt = 41.3 percent.

The acids obtained were acetic and butyric acids (the latter derived from the portion of the oil insoluble in water).

The silver salts were fractionally precipitated and analysed.

1st fraction. 0.061 gave 0.034 Ag. Ag = 55.7.

C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>Ag requires Ag = 55.4 per cent.

The last fraction. 0.0582 gave 0.0374 Ag. Ag = 64.3.

C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Ag requires Ag = 64.7 per cent.

The analyses of the platinichloride and aurichloride prove the existence in the first fraction of a substance of the formula C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>, whilst its general properties and its oxidation to ammonia, methylamine, and acetic acid, prove that it is a dimethylglyoxaline with one methyl group attached to nitrogen.

It therefore remains to be decided to which of the three carbon atoms the other methyl group is attached. Of the three isomerides possible, two are known and have been characterised (compare p. 464).

The constitution of 1:2-dimethylglyoxaline is definitely established, but that of the other synthetical dimethylglyoxaline is still uncertain; the dimethylglyoxaline derived from *isopilocarpine* is, however, *not* identical with it.

The following table shows the close similarity existing between the derivatives of these isomerides:

|                 |       | 1:2.     | 1:4 (or 1:5). | From<br><i>isopilocarpine</i> . |
|-----------------|-------|----------|---------------|---------------------------------|
| Base.....       | b. p. | 205—206° | 203°          | 210—215°                        |
| Aurichloride    | m. p. | 215°     | 215°          | 214—215°                        |
| Platinichloride | m. p. | 230°     | 238—239°      | 238—239°                        |
| Picrate .....   | m. p. | 179°     | 167°          | 167°                            |

The only difference between the 1:4(or 1:5)-isomeride and that from *isopilocarpine* is that the mixture of equal weights of their picrates, each melting at 167°, melts at 140—145°.

The glyoxalines are, therefore, isomeric and not identical. The constituent of the fraction, b. p. 100—120° under 10 mm. pressure, and soluble in water, is therefore 1:4(or 1:5)-*dimethylglyoxaline*.

#### *Identification of 1:4(or 1:5)-Methylamylglyoxaline.*

The attempted preparation of a crystalline hydrochloride from the fraction b. p. 150—160° under 10 mm. pressure being unsuccessful, the platinichloride was prepared as follows. The base was dissolved in alcohol, made faintly acid with aqueous hydrochloric acid, and platinic chloride in aqueous solution added. A yellow, crystalline precipitate separated, which was allowed to remain in contact with the solution until the latter began to darken, the crystals were then rapidly collected, washed, and dried.

*Methylamylglyoxaline platinichloride* forms light brownish-coloured, tabular crystals which melt at 198°. The melting point was not altered by further crystallisation. On analysis:

0.172 gave 0.0466 Pt. Pt = 27.1.

0.1092 „ 0.0298 Pt, 0.1254 CO<sub>2</sub>, and 0.0468 H<sub>2</sub>O. Pt = 27.3  
C = 31.3; H = 4.8.

0.124 gave 0.034 Pt, 0.1418 CO<sub>2</sub>, and 0.054 H<sub>2</sub>O. Pt = 27.4;  
C = 31.2; H = 4.8.

(C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>)<sub>2</sub>.H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 27.3; C = 30.3; H = 4.7 per cent.

The hydrochloride, obtained from the pure platinichloride by treatment with hydrogen sulphide, yielded a crystalline *picrate* melting at 134°, but an amorphous *aurichloride*. In 5 per cent. aqueous solution the hydrochloride was optically inactive.

The *methylamylglyoxaline*, obtained from the pure hydrochloride by



adding excess of potassium carbonate and extracting with ether, was a colourless, viscid oil with a feebly basic odour, insoluble in water:

0.1026 gave 0.2672  $\text{CO}_2$  and 0.0954  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 10.3$ .

0.1092 „ 0.2844  $\text{CO}_2$  „ 0.0982  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 10.0$ .

$\text{C}_9\text{H}_{16}\text{N}_2$  requires  $\text{C} = 71.1$ ;  $\text{H} = 10.5$  per cent.

*Oxidation of the Fraction, b. p. 145—160° under 10 mm., with Permanganate.*

This fraction, containing, besides methylamylglyoxaline, the substance boiling between it and dimethylglyoxaline and yielding butyric acid on oxidation, was oxidised with excess of permanganate, and the bases and acids isolated by the usual method.

The bases formed were identified as ammonia and methylamine; the platinichloride of the latter on analysis gave:  $\text{Pt} = 41.2$  (calculated  $\text{Pt} = 41.3$  per cent).

The acids formed were identified as *n*-hexoic and *n*-butyric acids.

The crude acids were purified by distillation, when three fractions were obtained: (1) a small fraction below 125°, chiefly ether, &c.; (2) 125—160°; (3) 160—190°. Only a slight residue was left in the distilling flask.

Fraction (2) smelt very strongly of butyric acid, whilst fraction (3) had a pleasanter smell and was more viscid.

*Fraction (2), b. p. 125—160°.*

The acid was converted into the barium salt and precipitated in two fractions with silver nitrate. The silver salts were analysed, with the following result:

1. 0.1176 gave 0.0656 Ag.  $\text{Ag} = 55.7$ .

2. 0.24 „ 0.1334 Ag.  $\text{Ag} = 55.6$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.4$  per cent.

The anilide, prepared in the usual way and recrystallised from ligroin, melted at 82°. *iso*Butyranilide melts at 102.5°, and butyranilide at 90°. The low melting point is due to the presence of the higher anilide which is sparingly soluble in ligroin, and is not easily separated. The corresponding acid was undoubtedly *n*-butyric acid.

*Fraction (3), b. p. 160—190°.*

The acid was converted into the silver salts by fractional precipitation in the usual manner, and on analysis:

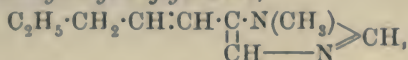
1. 0.114 gave 0.0546 Ag. Ag = 47.9.

2. 0.0364 „ 0.0178 Ag. Ag = 48.8.

$C_6H_{11}O_3Ag$  requires Ag = 48.4 per cent.

The anilide, prepared in the usual way and purified by recrystallisation from ligroin until of constant melting point, melted at 94—95°; *n*-hexoanilide melts at 95°. The acid was therefore *n*-hexoic acid.

The analyses of the pure base and platinichloride, and the products of oxidation, prove that one constituent of this fraction is methylamylglyoxaline, and from the fact that it is formed with 1:4(or 1:5)-dimethylglyoxaline, it may be inferred that the substituent groups occupy the same position in each case. With regard to the more volatile constituent of the fraction yielding butyric acid on oxidation, the analysis of the fraction boiling at 145—160° under 10 mm. pressure would indicate that it has the formula  $C_9H_{14}N_2$ . In this case it might be regarded as *methylamyleneglyoxaline*,



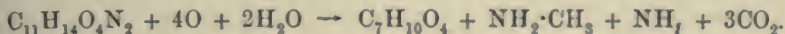
which, with permanganate, would oxidise at the double bond as well as the glyoxaline ring, giving *n*-butyric acid. The unsaturated nature of the compound would also account for its readiness to oxidise. This fraction (b. p. 145—160° under 10 mm. pressure) contains, therefore, 1:4(or 1:5)-*methylamylglyoxaline*, and probably 1:4(or 1:5)-*methylamyleneglyoxaline*.

*iso*Pilocarpine, when distilled with soda-lime, yields ammonia, methylamine, 1-methylglyoxaline, 1:4(or 1:5)-dimethylglyoxaline, 1:4(or 1:5)-methylamylglyoxaline, and probably 1:4(or 1:5)-methylamyleneglyoxaline.

#### *Oxidation of isoPilocarpinolactone.*

In order to determine the constitution of dibromo*isopilocarpinic* acid and of *isopilocarpinolactone*, the latter was oxidised with permanganate, and the resulting product treated in the same manner as in the case of *isopilocarpine*, in order to isolate the bases and acids formed.

Five grams of *isopilocarpinolactone* (m. p. 83°) dissolved in water were oxidised with a slight excess (9 grams) of permanganate in 1 per cent. aqueous solution. At 12°, the colour of the permanganate was immediately discharged until the above quantity had been added, when the slight excess remained unchanged. In this respect the lactone differs from *isopilocarpine*, where the colour is not discharged so readily. The amount of oxidising agent used agreed well with the following equation. Calculated 8.3 grams; required 9 grams.



The bases obtained were identified as ammonia and methylamine. The platinichloride of the latter was analysed.

0.109 gave 0.045 Pt. Found Pt = 41.3. Calculated Pt = 41.3 per cent.

The acid was isolated as the ethyl ester, which distilled completely at 160—170° under 20 mm. pressure; titration of this derivative showed that the acid was monobasic and lactonic.

After hydrolysis, 0.3886 ester required for neutralisation 2.2 c.c. *N*-alkali solution cold and 4.0 c.c. hot. Calculated for an acid  $C_7H_{10}O_4$  the requisite quantities are 2.1 c.c. and 4.2 c.c. respectively.

On hydrolysis, the acid was obtained as a colourless oil which quickly became solid. The crystals, after crystallisation from hot benzene, melted at 104°, and on analysis:

0.1052 gave 0.2044  $CO_2$  and 0.0616  $H_2O$ . C = 53.0; H = 6.5.

$C_7H_{10}O_4$  requires C = 53.2; H = 6.3 per cent.

The aqueous solution of the acid was dextrorotatory, and with barium carbonate yielded a barium salt which was analysed with the following result.

0.128 gave 0.066  $BaSO_4$ . Ba = 30.3.

$(C_7H_9O_4)_2Ba$  requires Ba = 30.4 per cent.

The acid was therefore pilopic acid.

The oxidation products of *isopilocarpinolactone* with permanganate solution are therefore ammonia, methylamine, and pilopic acid.

#### *Oxidation of Pilocarpine with Potassium Permanganate.*

Twenty grams of pure pilocarpine were oxidised with 63 grams of permanganate at the ordinary temperature, and the products of oxidation isolated as described under the oxidation of *isopilocarpine*.

The ethyl ester obtained was distilled under 10 mm. pressure, and the following fractions separated:

1. 165—175°      2. 175—180°      3. Above 180°.

The first fraction was analysed with the following result:

0.128 gave 0.277  $CO_2$  and 0.0918  $H_2O$ . C = 59.0; H = 8.0.

$C_{10}H_{16}O_4$  requires C = 60.0; H = 8.0 per cent.

These figures are almost identical with those previously obtained by Pinner and Kohlhammer (*Ber.*, 1900, 33, 1424).

When the ester was treated with excess of strong aqueous ammonia, the crystalline diamide of homopilopic acid (m.p. 208°) was obtained.

The second fraction was hydrolysed and the acid obtained titrated; in the cold, 0.42 required 24.4 c.c. normal alkali solution for neutralisation, and, when boiled with excess of alkali and titrated back with acid,



47.6 c.c. : calculated for an acid,  $C_8H_{12}O_4$ , the requisite quantities are 24.4 c.c. and 48.8 c.c. respectively.

The specific rotation in aqueous solution was determined with the following result :

$\alpha_D = +2.1^\circ$ ;  $l = 1$  dm.;  $c = 4.78$ ;  $[\alpha]_D = +43.9^\circ$ ; homopilocarpic acid has  $[\alpha]_D +45.4^\circ$ .

The barium salt was prepared in the usual way by neutralisation with barium carbonate :

0.393 gave 0.1914  $BaSO_4$ .  $Ba = 28.6$ .

$(C_8H_{11}O_4)_2Ba$  requires  $Ba = 28.6$  per cent.

When treated with ammonia, the third fraction yielded the diamide m. p.  $208^\circ$ , which furnished the following data :

0.0976 gave 0.1834  $CO_2$  and 0.0764  $H_2O$ .  $C = 51.2$ ;  $H = 8.7$ .

$C_8H_{16}O_3N_2$  requires  $C = 51.1$ ;  $H = 8.5$  per cent.

A determination of its specific rotation gave the following result :

$\alpha_D = +0.2^\circ$ ;  $l = 1$  dm.;  $c = 0.934$ ;  $[\alpha]_D = +21.4^\circ$ .

Pinner and Schwarz found for the amide (m. p.  $206^\circ$ )  $[\alpha]_D = +20.8^\circ$ . The above results prove conclusively that the oxidation product of pilocarpine with permanganate at the ordinary temperature consists almost entirely of homopilocarpic acid.

#### *Miscellaneous Experiments with isoPilocarpine.*

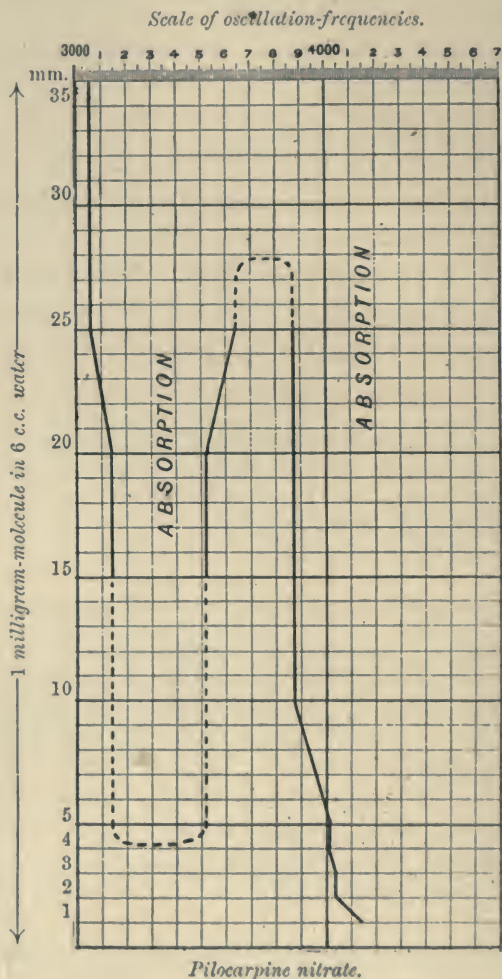
The extraordinary stability of *isopilocarpine* towards reducing agents has already been noticed, even sodium in boiling amyl-alcoholic solution failing to attack it. An attempt was therefore made to reduce it electrolytically by Tafel's method (*Ber.*, 1900, 33, 2209), but this was also unsuccessful.

Attempts were also made to form diacidic salts of *isopilocarpine*, first, by heating with excess of methyl iodide in a sealed tube for 2 hours at  $100^\circ$ , and, secondly, by heating with concentrated hydrochloric acid at  $180^\circ$ , but in both cases only the normal mono-acidic products were obtained.

In view of the suggestion by Pinner and Schwarz that the compounds previously described as methyl*isopilocarpine* derivatives were not such, but *isopilocarpine* methyl compounds, picric acid was added directly to an aqueous solution of *isopilocarpine* methiodide when a crystalline picrate was obtained (m. p.  $136^\circ$ ), identical with that previously described as methyl*isopilocarpine* picrate. As no change other than simple replacement of the iodine by the picric acid radical can be assumed, it follows that the substance described as methyl*isopilocarpine*

picrate is really *isopilocarpine* methyl picrate and that *isopilocarpine* contains the :N and not the :NH residue.

A previous attempt to titrate *isopilocarpine* not having given perfectly satisfactory results, the experiment was repeated:



0.1316 when boiled with excess of caustic alkali and titrated back with acid required, 6.8 c.c. decinormal soda for neutralisation, with phenolphthalein as indicator, the calculated amount being 6.3 c.c. *isoPilocarpine* behaved therefore as a normal lactone.

*The Absorption Spectra of Pilocarpine Nitrate and isoPilocarpine Nitrate.*

The absorption spectra of pilocarpine and *isopilocarpine* have been kindly determined for me by Prof. J. J. Dobbie, to whom I wish to express my hearty thanks. The results of his observations were as follows.

Pilocarpine nitrate is highly diactinic. It was necessary therefore to work with solutions much more highly concentrated than those usually employed in examining absorption spectra. Three independent series of observations were made with solutions of different strengths, and, so far as they were comparable, gave identical results. The measurements and curve give the results obtained with a solution containing 1 mg. mol. dissolved in 6 c.c. of water. There is one well-marked absorption band. The results obtained with *isopilocarpine* nitrate were identical with those obtained with pilocarpine nitrate; three independent series of observations being also made in the case of the former substance. The spectra of the two nitrates were identical (see p. 452).

## MEASUREMENTS.

*Pilocarpine Nitrate.*

| Thickness of layer of liquid in millimetres. | Description of spectrum.                  | $1/\lambda$ .       | $\lambda$ .         |
|--|---|---------------------|---------------------|
| 1 milligram-mol. in 6 c.c. of water.         |   |                     |                     |
| 35   | Spectrum transmitted to .....             | 3053                | 3275                |
| 30   | " " .....                                 | 3053                | 3275                |
| 25   | " " .....                                 | 3053                | 3275                |
|  | <b>Absorption band</b> .....              | <b>3053 to 3633</b> | <b>3275 to 2752</b> |
|  | Very weak spectrum .....                  | 3633 to 3880        | 2752 to 2577        |
| 20 and 15                                    | Spectrum transmitted to .....             | 3140                | 3185                |
|  | <b>Absorption band</b> .....              | <b>3140 to 3520</b> | <b>3185 to 2841</b> |
|  | Spectrum .....                            | 3520 to 3880        | 2841 to 2577        |
| 10   | Spectrum transmitted to .....             | 3880                | 2577                |
|  | Very weak in position of absorption band. |                     |                     |
| 5 and 4                                      | Spectrum transmitted to .....             | 4008                | 2495                |
|  | Weak in position of absorption band.      |                     |                     |
| 3 and 2                                      | Spectrum transmitted to .....             | 4040                | 2475                |
| 1  | " " .....                                 | 4133                | 2419                |



*Pilocarpine Nitrate (continued).*

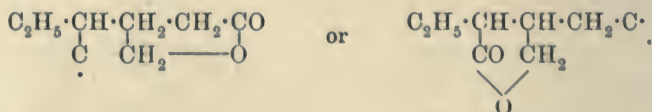
| Thickness of layer of liquid in millimetres. | Description of spectrum.      | $1/\lambda$ . | $\lambda$ . |
|--|-------------------------------|---------------|-------------|
| 1 milligram-mol. in 30 c.c. of water.        |                               |               |             |
| 5, 4 and 3                                   | Spectrum transmitted to ..... | 4133          | 2419        |
| 2  | " " .....                     | 4183          | 2391        |
| 1  | " " .....                     | 4250          | 2353        |
| 1 milligram-mol. in 150 c.c. of water.       |                               |               |             |
| 5, 4 and 3                                   | Spectrum transmitted to ..... | 4250          | 2353        |
| 2  | " " .....                     | 4340          | 2304        |
| 1  | " " .....                     | 4370          | 2288        |

The measurements for *isopilocarpine* nitrate are identical with those for *pilocarpine* nitrate.

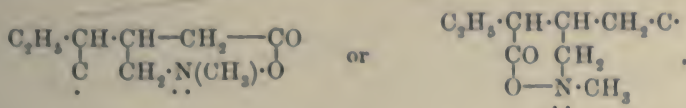
## DISCUSSION OF RESULTS.

*The Constitution of isoPilocarpine.*

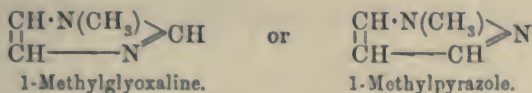
Since *isopilocarpine* on oxidation with potassium permanganate yields the potassium salt of a hydroxy-acid,  $C_8H_{14}O_5$ , of which homopilocarpic acid,  $C_8H_{12}O_4$ , is the lactonic acid, and as the constitutional formula of the hydroxy-acid has been determined with a high degree of probability to be  $C_2H_5 \cdot CH(CO_2H) \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$ , it is permissible to assume that *isopilocarpine* contains one of the following complexes:



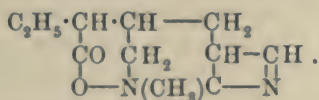
Since a formula containing either of these complexes would yield homopilocarpic acid on oxidation, it follows that either formula would be equally valid. There is also a third possibility to consider in connection with a formula for *isopilocarpine*, that is the existence of a betaine grouping in the molecule. If this were the case the following type of formula would account for the products of oxidation:



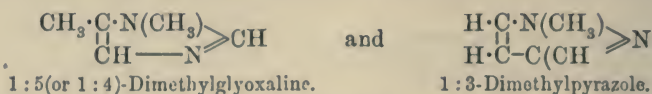
On oxidation the nitrogen atom is split off as methylamine and is replaced by hydroxyl, yielding homopilocarpic acid. In addition to the existence of one of the above complexes in the molecule the occurrence of the nitrogen atoms as  $\text{N}:$  and  $:\text{N} \cdot \text{CH}_3$  has been proved, and subtracting these groups from the empirical formula of isopilocarpine,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$ , the condition of two carbon and two hydrogen atoms remains to be explained. Assuming first that the two nitrogen atoms are present in the same complex, I have been able to construct only two possible formulæ for the group to be attached to the homopilocarpic residue, one being a glyoxaline and the other a pyrazole residue.



The homopilocarpic residue might be attached to any of the three carbon atoms in the ring by replacement of hydrogen, and the alkaloid would thus be a substituted glyoxaline or pyrazole. If, however, one of the nitrogen atoms, for example, that in the methylamine residue, is quinquivalent, the homopilocarpic complex must be attached to a ring containing one nitrogen atom, and, on these grounds, the following formula for the alkaloid might be suggested:



Besides these three possibilities there are also many others depending on the point of attachment of the two groups. The reactions of isopilocarpine which have been most thoroughly studied are (1) oxidation with permanganate, yielding ammonia, methylamine, homopilocarpic and lower acids, (2) bromination under varying condition with the formation of dibromoisopilocarpine or dibromoisopilocarpic acid, (3) behaviour towards alkyl iodides and the treatment of the quaternary ammonium compounds with caustic alkali, yielding methylamine and the respective alkylamine. These reactions would not enable us to decide between the three types of formulæ previously mentioned. In order to trace the analogy which might exist between isopilocarpine and glyoxaline or pyrazole derivatives, the following dimethyl-compounds of the latter have been prepared and their reactions studied (see pp. 465, 467):



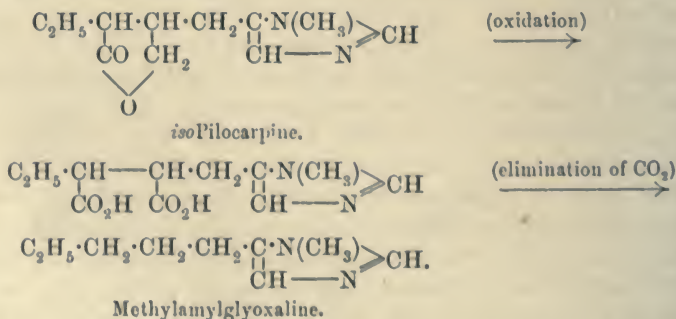
The results of the examination showed a remarkable analogy between the behaviour of *isopilocarpine* and that of dimethylglyoxaline, and a striking dissimilarity between that of *isopilocarpine* and dimethylpyrazole.

The results are shown in the following table :

| Reaction.                                    | Pyrazole.                         | Glyoxaline.                                    | isoPilocarpine.  |
|--|-----------------------------------|--|--|
| Oxidation with permanganate                  | { Pyrazole carb-<br>oxylic acid } | { Ammonia,<br>methylamine and<br>acetic acid } | { Ammonia, methyl-<br>amine and homo-<br>pilocarpic acid } |
| Bromination                                  | Dibromo-compound                  | Dibromo-compound                               | Dibromo-compound   |
| { Bromination at<br>100° }                   | { Dibromo-compound }              | { Acid containing<br>N and Br }                | { Dibromo <i>isopilo</i> -<br>carpinic acid }              |
| Methiodide with<br>caustic potash<br>at 180° | { Very slight reaction }          | { Methylamine and<br>acetic acid }             | { Methylamine and<br>homopilocarpic<br>acid }              |

These results amplify and confirm the analogy existing between pilocarpine and glyoxaline derivatives, first pointed out by Pinner and Schwarz (*loc. cit.*), and exclude any formula for pilocarpine or *isopilocarpine* containing a pyrazole ring. The glyoxaline formula for *isopilocarpine* suggested by the above-mentioned analogy receives conclusive proof from the formation of various glyoxaline derivatives by distillation of the alkaloid with soda-lime. The crude product thus formed has been proved to contain 1-methylglyoxaline, 1:4(or 1:5)-dimethylglyoxaline, 1:4(or 1:5)-methylamylglyoxaline and probably 1:4(or 1:5)-methylamyleneglyoxaline together with ammonia and methylamine. Their formation is most readily explained by supposing that the (CH<sub>2</sub>OH) group is oxidised to carboxyl with subsequent elimination of carbon dioxide yielding methylamylglyoxaline.

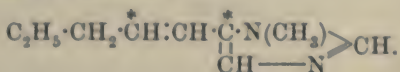
Assuming the following formula for *isopilocarpine*, the change might be thus represented.



The unsaturated methylamyleneglyoxaline is probably produced by

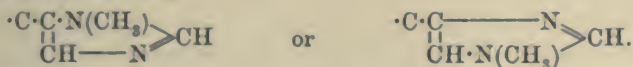


the elimination of water prior to the oxidation of the  $(\text{CH}_2\text{OH})$  group, and a change in the position of the double bond thus produced with subsequent oxidation and elimination of carbon dioxide, giving rise to the following glyoxaline.



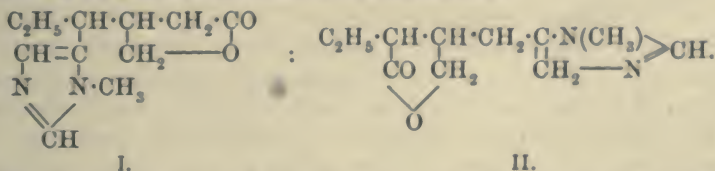
This compound oxidises at both the points marked with an asterisk, yielding butyric and carbonic acids, ammonia, and methylamine. The other glyoxalines, as well as ammonia and methylamine, are produced by further disruption of the molecule and the final fission of the glyoxaline ring itself. It has previously been shown that glyoxaline derivatives are very stable under similar conditions, for example, 2-methylglyoxaline was prepared by passing 1-methylglyoxaline through a red-hot tube (Wallach, *Ber*, 1883, 16, 542). These facts, taken in conjunction with the analogies shown to exist between isopilocarpine and glyoxaline derivatives, seem to afford conclusive evidence that isopilocarpine is a glyoxaline derivative, and accordingly the betaine formula suggested for isopilocarpine must be abandoned. The glyoxaline formula having been adopted, two problems remain for solution: (1) the determination of the point of attachment of the glyoxaline and homopiloc complexes, (2) choice of the appropriate formula for the homopiloc residue.

The identification of the dimethylglyoxaline formed with the 1:4- (or 1:5)-isomeride proves that one of the following complexes must exist in isopilocarpine.



Inasmuch as it is impossible at the present time to decide between these formulæ, during the remainder of the discussion it will be assumed that isopilocarpine is a 1:5-glyoxaline derivative. The arguments used are equally valid for a 1:4-formula, if this should prove to be correct.

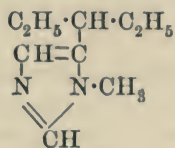
Assuming that isopilocarpine is a 1:5-glyoxaline derivative the following formulæ are possible for isopilocarpine:



The determination of the constitution of the methylamylglyoxaline formed renders it possible to decide between these two formulæ.

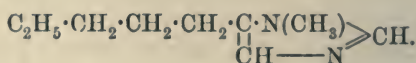
The formation of the methylamylglyoxaline can best be explained, as already indicated, by the oxidation of the (CH<sub>2</sub>OH) group to carbonyl and subsequent elimination of carbon dioxide.

The methylamylglyoxaline thus derived from formula I or II will have the following constitution:



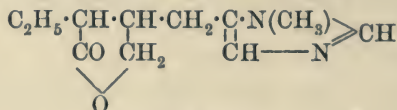
I.

or



II.

These compounds would yield on oxidation either (I) diethylacetic acid or (II) *n*-hexoic acid, besides ammonia and methylamine. The identification of the acidic product as *n*-hexoic acid justifies the adoption of formula II. From the experimental results recorded in this and previous papers and the deductions made therefrom, it is possible to propose the following constitutional formula for *isopilocarpine* with a considerable degree of certainty, although complete proof can be furnished by synthesis alone. The formula given is subject to the reservation previously mentioned.

*iso*Pilocarpine.

### *The Constitution of Pilocarpine.*

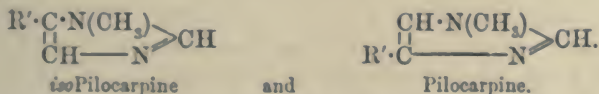
In former papers it was explained that, after having arrived at the constitution of *isopilocarpine*, the more stable of the two alkaloids, it might be possible from a consideration of its formula and a comparison of the two alkaloids to pass to the formula of pilocarpine. This procedure seemed also necessary, since in certain reactions, for example, fusion with caustic potash or distillation with soda-lime, the products obtained would be those produced from *isopilocarpine* and not from pilocarpine. Since *isopilocarpine* is formed from pilocarpine by simple means, such as heating alone or with water, the relationship must be a close one. Furthermore, since pilocarpine, by oxidation with permanganate, at ordinary temperatures, yields homopilocarpic acid, identical in all respects with that obtained from *isopilocarpine*, both alkaloids must contain this complex. The formation of homopilocarpic acid from pilocarpine might be thought to exclude the possibility of stereoisomerism, for the only asymmetric carbon atoms present are those in

the homopilopic complex and the glyoxalines obtained were optically inactive.

There are also two reactions in which the alkaloids apparently differ, which, as Pinner and Schwarz have pointed out, would favour the view of structural isomerism. These reactions are (1) the action of bromine under pressure, when, with pilocarpine, bromocarpinic acid,  $C_{10}H_{13}O_4N_2Br$ , is produced, whilst with isopilocarpine, dibromoisopilocarpinic acid,  $C_{11}H_{14}O_4N_2Br_2$ , is formed; (2) the action of chromic acid on pilocarpine leading to the formation of pilocarpoic acid,  $C_{11}H_{16}O_5N_2$ , whilst in the case of isopilocarpine, no definite product could be isolated, and the action seemed to result in the general disruption of the molecule.

If the alkaloids are structural isomerides, the difference must lie in the point of attachment of the homopilopic complex to the glyoxaline ring, since both alkaloids must contain the homopilopic residue, and from the very close relationship of the alkaloids and their method of conversion it is almost certain that both contain a glyoxaline ring.

The relationship would be shown thus, where  $R'$  = homopilopic complex:



These formulæ are, however, so nearly alike that they fail to explain the differences in the reactions previously mentioned. The mechanism of such an isomeric change is not easy to conceive, for, as it takes place by heat alone, it is most likely to occur by a migration either of the homopilopic residue to the contiguous carbon atom, or of the methyl group from one nitrogen atom to the other with rearrangement of the double linkings. A migration of the methyl group from the nitrogen to the contiguous carbon atom takes place in the formation of 2-methylglyoxaline by passing 1-methylglyoxaline through a red-hot tube,



but this cannot take place in the conversion of pilocarpine into isopilocarpine, since both alkaloids contain the  $:N \cdot CH_3$  group. The theory of structural isomerism therefore appears improbable.

If the alkaloids are stereoisomerides, this must be due to the asymmetric carbon atoms which occur only in the homopilopic residue. The formation of homopilopic acid from pilocarpine by oxidation can be readily explained when it is considered that the homopilopic acid is produced in the presence of free alkali and purified by the distillation of its ester, both of which factors would conduce to the formation of the stable modification.



With regard to the other two apparent differences, a satisfactory explanation can be offered of at least one of the reactions.

When bromine acts on pilocarpine or *isopilocarpine* under pressure, the crystalline compound isolated in each case is different, but it by no means follows that the reaction does not proceed similarly in both cases. It may be that more than one substance is formed, and that they differ in their ability to crystallise, just as pilocarpine methiodide is amorphous whilst *isopilocarpine* methiodide is crystalline. Further, I have previously shown (Trans., 1901, 79, 598) that there is experimental evidence that the reactions are similar, and that dibromopilocarpinic acid might be present in the mother liquors from which bromocarpinic acid has crystallised, just as bromo*isocarpinic* acid might be present in the filtrates from which dibromo*isopilocarpinic* acid has been obtained. The yield of crystalline acid obtained is in harmony with this suggestion. The reaction of the alkaloids with chromic acid has not been sufficiently studied to permit of any deductions being made in support of either theory.

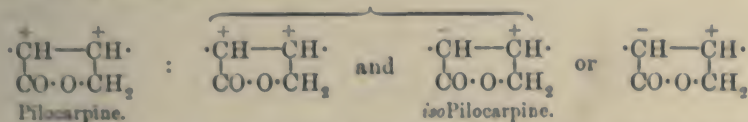
A consideration of the specific rotation of pilocarpine and its derivatives affords support both for the theory of the stereoisomerism of the alkaloids and also for the constitutional formula proposed. In the cases of pilocarpine, *isopilocarpine*, homopilopie acid, and pilopie acids it has been noted that the specific rotation of the substances in alkaline solution is much less than in aqueous solution. This is in harmony with the general rule of the specific rotation of lactones in alkaline and aqueous solution, and the gradual change in the specific rotation of an aqueous solution of pilocarpine, from  $+100^\circ$  to  $+77^\circ$  is undoubtedly due to the opening of the lactone ring.

Three possible explanations as to the nature of the stereoisomerism may be briefly mentioned.

1. The fact that the conversion of pilocarpine into *isopilocarpine* is accompanied by a change in the specific rotation from  $+100.5^\circ$  to  $+42.8^\circ$  suggests that partial racemisation may be the cause of the isomeric change. Of the two asymmetric carbon atoms in *isopilocarpine*, one is attached to a carboxyl residue, whilst the other is attached to a methylene group. In accordance with general views on this subject, it may be assumed that the first of these asymmetric carbon atoms undergoes inversion, and that the optical activity of *isopilocarpine*, homopilopie and pilopie acids is due to the carbon atom attached to the  $-\text{CH}_2-$  group. Many examples of this type of change could be quoted, but it will be sufficient to refer to the example given by Pasteur of the change of quinine into quinicine.

2. That pilocarpine contains two non-equivalent asymmetric carbon atoms, and that in the formation of *isopilocarpine* complete inversion of the asymmetric carbon atom attached to the carboxyl residue takes

place. The relation between pilocarpine and *isopilocarpine* might then be represented as follows:



In the latter case, the specific rotation of *isopilocarpine* would be the difference between the rotatory powers of the two asymmetric carbon atoms, and *isopilocarpine* would be incapable of resolution.

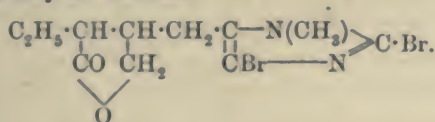
3. That, in addition to either of the above causes of isomerism, the bases may be also geometrical isomerides, corresponding to *cis*- and *trans*-modifications. The difference in the melting points of the salts and in the stability of pilocarpic and *isopilocarpic* acids (Pinner and Schwarz, *Ber.*, 1902, 35, 201) tends to support this view.

These conclusions are also supported by the fact that the alkaloids, pilocarpine and *isopilocarpine*, give absolutely identical absorption spectra, and it has been shown (Hartley, *Phil. Trans.*, 1885, ii, 471) that stereoisomeric alkaloids give identical spectra, whilst any considerable difference in structure is accompanied by a corresponding difference in the absorption spectra.

In view of all these facts, it seems most probable that pilocarpine and *isopilocarpine* are stereoisomerides, and must therefore be represented by the same structural formula.

#### *Formulae of various Derivatives of Pilocarpine and isoPilocarpine.*

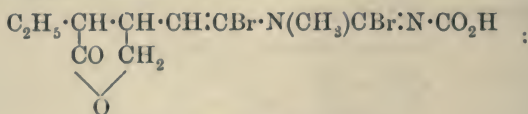
*Dibromopilocarpine and isoPilocarpine.*—From the analogy with the glyoxalines examined there can be no doubt that substitution takes place in the glyoxaline ring, and the constitutional formulæ of each of these substances may be written:



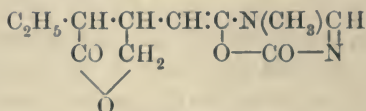
*Dibromoisopilocarpinic Acid and isoPilocarpinolactone.*—The constitution of these two substances can be proposed with a great degree of certainty from the formation of ammonia, methylamine, and pilopic acid by the oxidation of *isopilocarpinolactone* and from the formation of pilopic acid by the action of sodium and alcohol on *dibromoisopilocarpinic acid* (*Trans.*, 1901, 79, 592).

The formation of pilopic acid proves the existence of the pilopic complex in these substances, and the oxidation must therefore have taken place in the glyoxaline ring.

The following formulæ are proposed :

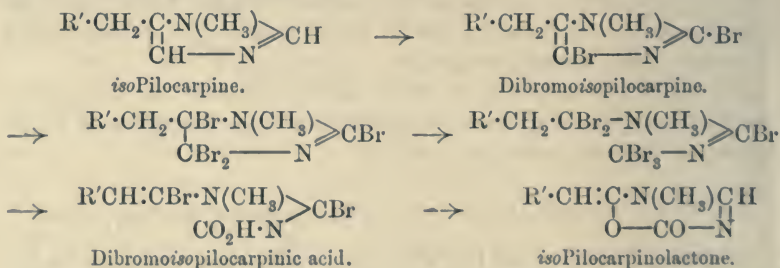


Dibromoisopilocarpinic acid.

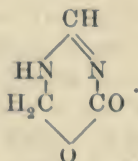


isoPilocarpinolactone.

The mode of formation of these substances may be explained by assuming that bromination first takes place with formation of dibromoisopilocarpine, which unites with excess of bromine with disruption of the double bond and formation of a tribromo-acid, this product then losing HBr, yielding dibromoisopilocarpinic acid. The stages in the reaction may be expressed in the following manner, where R' = the pilopic residue.



These formulæ explain perfectly the formation of pilopic instead of homopilopic acid on oxidation and the greater readiness to oxidise with permanganate, as well as the formation of ammonia and methylamine and the other characters of these compounds. If these formulæ are correct, and they are strongly supported by experimental evidence, then isopilocarpinolactone must be regarded as the first member of a new type of ring compounds of which the parent substance would be

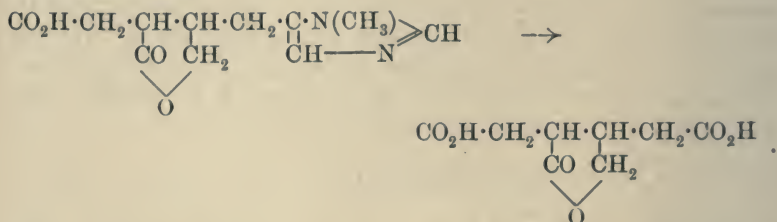


Preliminary experiments on the action of bromine under pressure on dimethylglyoxaline (p. 467) indicate that a similar reaction occurs with other derivatives of glyoxaline, and this change will be further





amine residue. If the former were oxidised, pilocarpoic acid on oxidation with permanganate should yield a dibasic and lactonic acid having the formula  $C_8H_{10}O_6$ , the glyoxaline ring undergoing oxidation in the usual way:



This, however, is not the case, as pilomalic acid,  $C_7H_{12}O_5$ , is dibasic. If the methyl of the methylamine residue were oxidised, then pilocarpoic acid on oxidation with permanganate should yield homopilopic acid, which again does not occur. Furthermore, both of these reactions are, *a priori*, extremely unlikely.

The explanation of Pinner and Schwarz is therefore quite untenable, and in the absence of any information as to the reactions of these acids no suggestions as to their constitution can be offered.

In conclusion, it may be pointed out that pilocarpine and isopilocarpine are the first and only known members of a new class of alkaloids, containing a glyoxaline ring.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

## L.—*Preparation and Properties of 1:4(or 1:5)-Dimethylglyoxaline and 1:3-Dimethylpyrazole.*

By HOOPER ALBERT DICKINSON JOWETT and CHARLES ETTY POTTER.

DURING the course of the investigation by one of us on the constitution of pilocarpine (see preceding paper), it was found necessary for the purpose of comparison to prepare certain derivatives of 1-methylglyoxaline and 1-methylpyrazole. Accordingly, 1:4(or 1:5)-dimethylglyoxaline and 1:3-dimethylpyrazole have been prepared and characterised, and their behaviour with certain reagents studied.

1:4(or 1:5)-*Dimethylglyoxaline* was prepared from 4(or 5)-methylglyoxaline, which in turn was obtained from the corresponding mercaptan according to the method of Gabriel and Pinkus (*Ber.*, 1893, 26, 2203). This latter base, which had hitherto been described as a liquid, was obtained in crystals melting at  $55^\circ$ . The new base is a liquid forming crystalline salts. With bromine at the ordinary

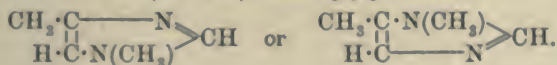
temperature, it forms a crystalline dibromo-derivative, but with excess of the reagent at 100° under pressure, further action occurs, a crystalline acid containing both nitrogen and bromine being formed. Chromic acid does not attack the base, but potassium permanganate oxidises it, producing ammonia, methylamine, and acetic acid. When the methiodide is heated with aqueous caustic potash in a sealed tube at 180°, methylamine and acetic acid are formed.

1:3-Dimethylpyrazole was prepared through its methiodide from 3-methylpyrazole, which was obtained by the condensation of formylacetone with hydrazine (Knorr and Macdonald, *Annalen*, 1894, 279, 225). Knorr also obtained this base (*loc. cit.*, 231), but had doubts as to its purity, and did not further investigate it. The base is a colourless liquid forming crystalline salts. With bromine, either at the ordinary temperature or at 100° under pressure, the dibromo-derivative is formed; in the latter respect, the base differs from the isomeric glyoxaline, which is decomposed by excess of bromine at 100°. With potassium permanganate, the corresponding pyrazolemonocarboxylic acid is formed, and the methiodide is not readily decomposed by aqueous caustic potash; in both these reactions the pyrazole behaves differently from the glyoxaline.

Professor C. R. Marshall has examined these compounds physiologically, but neither of them was found to possess any action analogous to that of pilocarpine. It was also found necessary to characterise the isomeric 1:2-dimethylglyoxaline which had been previously prepared (*Ber.*, 1883, 16, 448), inasmuch as the physical constants of its salts had not been recorded.

#### EXPERIMENTAL.

1:4(or 1:5)-Dimethylglyoxaline,



This base was prepared from 4(or 5)-methylglyoxaline by the method (B) given by Titherley for the preparation of monoalkyl-substituted amides (*Trans.*, 1901, 79, 401); it was, however, extracted with ether instead of with benzene. The dark-coloured and oily residue, which was distilled under 20—25 mm. pressure, boiled almost entirely between 110° and 117°, the yield being 60 to 70 per cent. of the theoretical. The product was rectified, and a fraction boiling at 116° under 25 mm. pressure analysed with the following result:

0.1058 gave 0.2426 CO<sub>2</sub> and 0.0824 H<sub>2</sub>O. C = 62.5; H = 8.6.

0.1250 „ 0.2850 CO<sub>2</sub> „ 0.0962 H<sub>2</sub>O. C = 62.2; H = 8.5.

0.0808 „ 20 c.c. nitrogen at 14° and 747 mm. N = 28.9.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub> requires C = 62.5; H = 8.3; N = 29.2 per cent,



The base, which distilled at  $203^{\circ}$  under the ordinary pressure, is a colourless liquid, soluble in water, alcohol, and ether in all proportions, and has a characteristic odour recalling both that of pyridine and of trimethylamine; it has a sp. gr. 1.003 at  $15^{\circ}/15^{\circ}$ .

1:4(or 1:5)-Dimethylglyoxaline was obtained by the following methods: (i) by the action of methyl iodide on the silver derivative of 4(or 5)-methylglyoxaline, in methyl-alcoholic solution, in a sealed tube at  $160^{\circ}$ ; (ii) by the action of sodium methyl sulphate on the sodium derivative of the methylglyoxaline in boiling amyl-alcoholic solution; but in neither of these two cases was the yield of dimethyl compound so satisfactory as in the method just described.

The *aurichloride* formed yellow needles, which, when crystallised from alcohol, melted at  $176^{\circ}$ , but after remaining in a desiccator over sulphuric acid for two or three days, the crystals melted at  $214\text{--}215^{\circ}$ .

The *picrate* immediately crystallised in long, yellow needles, which, after crystallisation from hot water, melted sharply at  $167^{\circ}$ , and were not altered by further crystallisation.

The *platinichloride* slowly separated from solution in orange-coloured, laminar crystals, which, after recrystallisation, melted and decomposed at  $239^{\circ}$ :

0.0972 gave 0.032 Pt. Pt = 32.9.

$(C_5H_8N_2)_2, H_2PtCl_6$  requires Pt = 32.4 per cent.

The *hydrochloride* was obtained on evaporating the aqueous solution in a vacuum over caustic potash, as a mass of very hygroscopic, colourless crystals melting at  $145^{\circ}$ .

The *methiodide* was prepared by heating the 4(or 5)-methylglyoxaline in a sealed tube at  $110^{\circ}$  for 3 or 4 hours with methyl iodide and methyl alcohol. On evaporation, the methiodide of dimethylglyoxaline slowly crystallised. It was redissolved in absolute alcohol, boiled with animal charcoal, filtered, and dry ether cautiously added to the solution while still warm, when the methiodide crystallised in fine needles. This operation was repeated until the product was colourless, and the melting point constant at  $156^{\circ}$ :

0.2538 gave 0.2494 AgI. I = 53.1.

$C_5H_8N_2, CH_3I$  requires I = 53.3 per cent.

#### *Action of Bromine.*

(1) *In Acetic Acid Solution.*—Dibromodimethylglyoxaline was prepared in a similar manner to dibromoisopilocarpine (Trans., 1901, 79, 580), and formed long, colourless needles, which melted sharply at  $127^{\circ}$ , and are soluble in alcohol and ether, but insoluble in water:

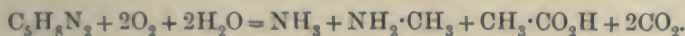
0.1416 gave 0.2103 AgBr. Br = 63.2.

$C_5H_8N_2Br_2$  requires Br = 63.0 per cent.

An attempt to reduce a small quantity of dibromodimethylglyoxaline with sodium and amyl alcohol gave a negative result.

(2) *In Aqueous Solution under Pressure.*—A preliminary experiment on a small quantity of dimethylglyoxaline showed that with excess of bromine in aqueous solution at  $100^\circ$  under pressure, no dibromodimethylglyoxaline was formed, but a crystalline acid was produced, containing both nitrogen and bromine, together with small quantities of ammonia and methylamine. The reaction will be further studied.

*Oxidation with Potassium Permanganate.*—2.5 grams of dimethylglyoxaline were oxidised with potassium permanganate at the ordinary temperature, and the products of the reaction isolated in the usual manner. The colour of the permanganate was not discharged immediately, but disappeared on allowing the mixture to stand a short time. The reaction may be represented by the equation :

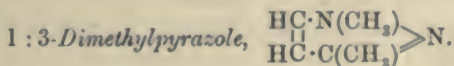


The amount of permanganate required, according to this equation, should be 11 grams, the amount actually used was 11.2 grams.

The bases formed were identified as ammonia and methylamine, the yield being theoretical; the platinichloride of the latter was isolated and analysed (Pt = 41.1 per cent.).

The acid formed was identified as acetic acid by the formation of ethyl acetate. The products of this oxidation are therefore ammonia, methylamine, and acetic acid.

*Action of Aqueous Caustic Potash on the Methiodide.*—Dimethylglyoxaline methiodide was heated with 20 per cent. caustic potash in a sealed tube at  $180^\circ$ , and the products of the reaction, which were isolated in the usual manner, were identified as acetic acid and methylamine, the latter being isolated in the form of its platinichloride (Pt = 40.9 per cent.).



1 : 3-Dimethylpyrazole was prepared from 3-methylpyrazole by the agency of the methiodide as follows. Ten grams of 3-methylpyrazole were dissolved in methyl alcohol, 34.5 grams of methyl iodide added, and the mixture heated in a sealed tube at  $110^\circ$  for 4 or 5 hours. When cold, a large quantity of crystalline dimethylpyrazole methiodide separated, this product being collected and washed with alcohol and

ether. The mother liquor, when treated with ether, gave a further quantity of methiodide, the total yield being almost quantitative.

The methiodide, when purified by repeated crystallisation from alcohol and ether, forms white, prismatic needles which melt at  $256^{\circ}$ ; it is very soluble in water and ethyl alcohol, less so in methyl alcohol, and quite insoluble in ether:

0.2374 required 10 c.c.  $N/10$   $\text{AgNO}_3$ .  $I = 53.5$ .

$\text{C}_5\text{H}_8\text{N}_2\text{CH}_3\text{I}$  requires  $I = 53.3$  per cent.

When subjected to dry distillation, the methiodide fused and decomposed, giving the dimethylated base and methyl iodide. The base was separated from a certain amount of methiodide, which volatilised, by treating the distillate with dry ether, filtering, drying over potassium carbonate, and redistilling. After removing the ether, nearly all the residue distilled between  $140^{\circ}$  and  $150^{\circ}$ , the yield being theoretical. After twice fractionating, a portion boiling at  $148^{\circ}$  was analysed. It was a colourless, mobile liquid with a slight pyridine-like odour, and a burning taste; it was quite neutral to litmus, and had a sp. gr. = 0.965 at  $15^{\circ}/15^{\circ}$ .

0.1352 gave 0.3084  $\text{CO}_2$  and 0.1032  $\text{H}_2\text{O}$ .  $C = 62.2$ ;  $H = 8.5$ .

0.1062 „ 0.2440  $\text{CO}_2$  „ 0.0812  $\text{H}_2\text{O}$ .  $C = 62.5$ ;  $H = 8.5$ .

0.0610 „ 14.6 c.c. nitrogen at  $11^{\circ}$  and 768 mm.  $N = 28.8$ .

$\text{C}_5\text{H}_8\text{N}_2$  requires  $C = 62.5$ ;  $H = 8.3$ ;  $N = 29.2$  per cent.

The *aurichloride*, prepared in the ordinary way, crystallised in yellow needles, which softened at  $165^{\circ}$  and fused completely at  $175^{\circ}$ . The salt contains two molecules of water of crystallisation, which are lost, together with a molecule of hydrochloric acid, on heating at  $115^{\circ}$ :

0.1302 air-dried salt lost at  $115^{\circ}$  0.0188 and gave 0.055 Au.

Loss in weight = 14.4; Au = 42.2.

$\text{C}_5\text{H}_8\text{N}_2\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$  requires Au = 41.8 and for loss of  $2\text{H}_2\text{O}, \text{HCl}$  15.2 per cent.

The *platinichloride* formed orange-coloured cubes which melted at  $234^{\circ}$ .

The *hydrochloride*, obtained by evaporating the aqueous solution in a vacuum over caustic potash, separated in very hygroscopic, long, prismatic crystals; it contained one molecule of water of crystallisation and melted at  $160^{\circ}$ , but dissociated slowly on heating at  $100^{\circ}$ :

0.02 required 13.2 c.c.  $N/10$   $\text{Na}_2\text{CO}_3$ ;  $\text{C}_5\text{H}_8\text{N}_2\text{HCl} \cdot 2\text{H}_2\text{O}$  requires 13.9 c.c.



*Action of Bromine.*

(1) *In Acetic Acid Solution.*—Dibromodimethylpyrazole, which was prepared in the same manner as the dibromodimethylglyoxaline, formed long, white needles melting at  $74^{\circ}$ ; these were very soluble in ethyl or methyl alcohol, and in ether or acetone, but insoluble in water:

0.2018 gave 0.3010 AgBr. Br = 63.4.

$C_5H_6N_2Br_2$  requires Br = 63 per cent.

(2) *In Aqueous Solution under Pressure.*—This reaction was found to yield the same product as the previous one.

Attempts to reduce the dibromodimethylpyrazole with zinc dust and glacial acetic acid, and also with sodium and boiling amyl alcohol, were unsuccessful.

*Oxidation with Potassium Permanganate.*

Dimethylpyrazole on oxidation with permanganate at  $80^{\circ}$  yielded no volatile base, but an acid forming colourless laminar crystals melting at  $222^{\circ}$ . The crystals were moderately soluble in hot water, and almost insoluble in cold:

0.1266 gave 0.2208  $CO_2$  and 0.0554  $H_2O$ . C = 47.6; H = 4.8.

$C_5H_6O_2N_2$  requires C = 47.6; H = 4.8 per cent.

The product of oxidation was therefore *N*-methylpyrazolemono-carboxylic acid,  $\begin{array}{c} \text{CH}-\text{N}(\text{CH}_3) \\ | \\ \text{CH}\cdot\text{C}(\text{CO}_2\text{H}) \end{array} \gg \text{N}$ .

*Action of Caustic Potash under Pressure on the Methiodide.*

This experiment was carried out in the usual manner, but as the amount of volatile bases formed was so minute, it was evident that the reaction had not taken place so readily or so completely as was the case with the glyoxaline; it was therefore not further investigated.

1:2-Dimethylglyoxaline,  $\begin{array}{c} \text{CH}\cdot\text{N}(\text{CH}_3) \\ | \\ \text{CH}-\text{C}-\text{N} \end{array} \gg \text{C}\cdot\text{CH}_3$ .

This compound was prepared in a precisely similar manner to that given above for the preparation of 1:4(or 1:5)-dimethylglyoxaline, that is, by the action of the sodium derivative of 2-methylglyoxaline on sodium methyl sulphate.

A fraction boiling at  $205\text{--}206^{\circ}$  was analysed with the following result:

0.1124 gave 0.2566  $\text{CO}_2$  and 0.0842  $\text{H}_2\text{O}$ ;  $\text{C} = 62.3$ ;  $\text{H} = 8.3$ .

$\text{C}_5\text{H}_8\text{N}_2$  requires  $\text{C} = 62.5$ ;  $\text{H} = 8.3$  per cent.

The *aurichloride*, when recrystallised from dilute hydrochloric acid, formed orange-yellow needles which melted at  $215^\circ$ :

0.0932 salt dried at  $100^\circ$  gave 0.0426 Au.  $\text{Au} = 45.7$ .

$\text{C}_5\text{H}_8\text{N}_2 \cdot \text{HAuCl}_4$  requires  $\text{Au} = 45.3$  per cent.

The *platinichloride*, recrystallised from dilute hydrochloric acid, formed orange-coloured needles which melted sharply and decomposed at  $230^\circ$ .

The *picrate*, which crystallised from hot water in fine, yellow, prismatic needles melting at  $179^\circ$ , was unchanged by further crystallisation from alcohol.

The *methiodide*, prepared by adding methyl iodide to the base, became solid immediately, with the evolution of much heat. When recrystallised from methyl alcohol and ether, it was obtained in white needles, which although slowly decomposed in the air, were not very hygroscopic, and did not melt below  $300^\circ$ .

In conclusion, we wish to reserve for future study the action of bromine under pressure on these glyoxalines.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

## LI.—The Rate of Decomposition of Diazo-compounds. Part III. The Temperature Coefficient.

By JOHN CANNELL CAIN and FRANK NICOLL.

THE study of the rate of decomposition of diazo-compounds affords an interesting example of the influence of temperature on the speed of chemical reactions. In our former papers on this subject (Part I, Trans., 1902, 81, 1412; Part II, 1903, 83, 206), we have recorded the values of the constant  $C$ , calculated from the formula  $\frac{1}{t} \log \frac{A}{A-x} = C$ , for a number of diazo-compounds at various temperatures.

An examination of these constants in each case shows a rapid increase in magnitude with rise in temperature, the numbers becoming three to four times larger for an increase of  $10^\circ$  (compare Euler, *Annalen*, 1902, 325, 301; also the table in van't Hoff's *Vorlesungen I*, 2nd Ed., 225).

By using Arrhenius's formula (*Zeit. physikal. Chem.*, 1889, 4, 227) for the temperature-coefficient, namely,

$$C_{t_1} = C_{t_0} \cdot e^{A(T_1 - T_0) : T_1 T_0},$$

we have calculated the values of the coefficient  $A$ , using the constants previously recorded.

In the following tables, the first two columns contain the values of

| Temperature.                          | $C$ .    | $t_0$ . | $t_1$ .   | $A$ .  | Divergence from the mean value. |
|---------------------------------------|----------|---------|-----------|--------|---------------------------------|
| <i>Diazobenzene chloride.</i>         |          |         |           |        |                                 |
| 20°                                   | 0·00072  | 20°     | 30°       | 12,520 | + 228                           |
| 30                                    | 0·00295  | 30      | 40        | 10,330 | - 1962                          |
| 40                                    | 0·00877  | 40      | 50        | 12,370 | + 78                            |
| 50                                    | 0·0298   | 50      | 60        | 13,950 | + 1658                          |
| 60                                    | 0·109    |         |           |        |                                 |
|                                       |          |         | Mean..... | 12,292 |                                 |
| <i>Diazo-o-toluene chloride.</i>      |          |         |           |        |                                 |
| 20°                                   | 0·00187  | 20°     | 30°       | 11,800 | - 903                           |
| 30                                    | 0·00706  | 30      | 40        | 11,530 | - 1173                          |
| 40                                    | 0·0238   | 40      | 50        | 14,780 | + 2077                          |
| 50                                    | 0·1027   |         |           |        |                                 |
|                                       |          |         | Mean..... | 12,703 |                                 |
| <i>Diazo-m-toluene chloride.</i>      |          |         |           |        |                                 |
| 20°                                   | 0·002085 | 20°     | 30°       | 10,700 | - 845                           |
| 30                                    | 0·00696  | 30      | 40        | 12,390 | + 845                           |
| 40                                    | 0·0257   |         |           |        |                                 |
|                                       |          |         | Mean..... | 11,545 |                                 |
| <i>Diazo-p-toluene chloride.</i>      |          |         |           |        |                                 |
| 30°                                   | 0·000209 | 30°     | 40°       | 14,840 | + 810                           |
| 40                                    | 0·000999 | 40      | 50        | 12,900 | - 1130                          |
| 50                                    | 0·00358  | 50      | 60        | 13,010 | - 1020                          |
| 60                                    | 0·0120   | 60      | 70        | 15,370 | + 1340                          |
| 70                                    | 0·0461   |         |           |        |                                 |
|                                       |          |         | Mean..... | 14,030 |                                 |
| <i>Diazobenzene-p-sulphonic acid.</i> |          |         |           |        |                                 |
| 60°                                   | 0·00633  | 60°     | 80°       | 14,200 | —                               |
| 80                                    | 0·0709   |         |           |        |                                 |
| <i>Diazo-m-nitrobenzene chloride.</i> |          |         |           |        |                                 |
| 80°                                   | 0·00314  | 80°     | 100°      | 15,380 | —                               |
| 100                                   | 0·0325   |         |           |        |                                 |



$C$  at the various temperatures, the third and fourth the temperatures from which we obtain the values of  $A$  in the fifth column.

The above values of  $A$  agree with those found by Euler (*loc. cit.*) for diazobenzene chloride (11,905), and diazo-*p*-bromobenzene chloride (13,634).

By the help of these numbers, we may calculate the value of  $C$  at any temperature, and hence, by the method shown in the first part of this work (*loc. cit.*, 1436), the amount of decomposition at the end of any given period of time.

In order to compare our results with those obtained by other chemists at different temperatures, we have calculated the values of  $C$  at these temperatures, using the mean value for  $A$  in each case.

For diazobenzene chloride, we thus obtain:  $C_{15} = 0.00035$  and  $C_{25} = 0.00145$ . Euler (*loc. cit.*) found 0.00031 and 0.00122 respectively, whilst Hantzsch (*Ber.*, 1900, 33, 2517) gives 0.00068 for  $C_{25}$ .

Diazo-*o*-toluene chloride has  $C_{25} = 0.00387$ . Euler found 0.0035. Diazo-*m*-toluene chloride has  $C_{25} = 0.0040$ . Euler found 0.0037. Diazo-*p*-toluene chloride has  $C_{25} = 0.000096$ . Hantzsch gives 0.000081. Diazobenzene-*p*-sulphonic acid has  $C_{64} = 0.0105$ . Hausser and Muller (*Compt. rend.*, 1892, 114, 549) give 0.0106.

Our calculated values are thus in very close agreement with the results of other observers, but Hantzsch's figures (from determinations by Osswald) are considerably lower than those found by both Euler and ourselves.

MUNICIPAL TECHNICAL SCHOOL,  
BURY, LANCASHIRE.

## LII.—*The Catalytic Racemisation of Amygdalin.*

By JAMES WALLACE WALKER.

IN a communication to the Royal Society of Canada in May, 1902, it was shown by the author and another that, under certain conditions, amygdalin yields, on hydrolysis, inactive mandelic acid instead of the *lævo*-variety. The latter is obtained, along with ammonium chloride and dextrose, when amygdalin is heated with concentrated hydrochloric acid. This result furnishes, as is well known, one of the arguments for ascribing to the glucoside the constitutional formula  $\text{CHPh(M)·CN}$ , where M represents a disaccharide radicle, most probably maltose (E. Fischer, *Ber.*, 1895, 28, 1510). The change consists in a reaction between amygdalin and water leading to the formation

of *l*-mandelic acid,  $\text{CHPh}(\text{OH})\cdot\text{CO}_2\text{H}$ , the essential product from the point of view of this research. When amygdalin is boiled with a dilute aqueous solution of an alkali, it is converted into a salt of amygdalinic acid,  $\text{CHPh}(\text{M})\cdot\text{CO}_2\text{H}$  (Liebig and Wöhler, *Annalen*, 1837, 22, 11). From analogy, it might be expected that aqueous hydrochloric acid would hydrolyse amygdalinic acid into dextrose and *l*-mandelic acid. And since even dilute hydrochloric acid could be employed without fear of benzaldehyde being produced—as happens when amygdalin and dilute hydrochloric acid are heated together—it was anticipated that by this method the yield of *l*-mandelic acid would be better than that obtained by the direct hydrolysis of amygdalin with strong hydrochloric acid. Instead of yielding the active acid, however, amygdalinic acid gave invariably inactive mandelic acid, both when caustic potash and baryta were used in its preparation and also when it was hydrolysed in daylight or in darkness with hydrochloric acid varying in strength from seminormal to concentrated. The phenomenon seemed of the same nature as several which have been recorded where racemisation takes place when an atom or group directly attached to an asymmetric carbon atom is replaced by another radicle. Besides the supposed analogy to similar cases, however, this one possesses a special interest because, if the racemisation of amygdalinic acid takes place when the maltose radicle is replaced by hydroxyl, some as yet unknown influence must be at work to prevent racemisation when the same substitution is being effected by the same agent under the same conditions in the molecule of amygdalin. The study of the reaction has therefore been continued, and the results show that most probably racemisation does not take place either during the course of substitution of the maltose radicle, or when the nitrile is being hydrolysed to carboxyl. On the contrary, it is effected, without any apparent chemical action, whenever amygdalin is dissolved in dilute alkaline solutions. Whether the immediate product of this change is racemic amygdalin or not is not yet absolutely certain, since the substance is non-crystalline and its aqueous solution evaporates to a gum not easily purified for analysis, but the experimental results are readily explained on this assumption; moreover, the amygdalinic acid of Liebig and Wöhler (*loc. cit.*) is racemoid as regards its mandelic asymmetric carbon atom, whilst its *lævo*-isomeride, possessed of a much higher degree of optical activity, is to be obtained by the partial hydrolysis of amygdalin with strong hydrochloric acid. The isolation and further study of these substances is in progress.

## EXPERIMENTAL.

The method adopted was to examine polarimetrically the rate of progress of the various reactions involved. The specific rotation of the amygdalin was determined in aqueous solution at  $20^{\circ}$ :

$$l = 1 \text{ dm.}, c = 10, \alpha_D = -3.54^{\circ}, \text{ hence } [\alpha]_D^{20} = -35.4^{\circ}.$$

$$\text{,, } 2 \text{ ,, ,, } 4, \text{ ,, } -2.915^{\circ}, \text{ ,, ,, } -36.45^{\circ}.$$

The rotatory power therefore changes but slightly with the concentration. The transformation of amygdalin into amygdalinic acid by treatment with aqueous baryta is a reaction which proceeds very readily. The baryta solution contained 2.338 grams of  $\text{Ba}(\text{OH})_2$  in 100 c.c., and 25 grams of amygdalin were dissolved in 250 c.c. of solution. After filtration, the reading in a 1 dm. tube was  $-4.3^{\circ}$ . A portion was heated on a boiling water-bath for 10 minutes under a reflux condenser, cooled, and again examined. The observed angle was now  $-5.75^{\circ}$ , and it showed no further change after heating for 30 minutes longer. After remaining at  $20^{\circ}$  for 6 days, the rotation of the solution was found to have changed to  $-5.75^{\circ}$ ; hence, in this case also, the reaction was complete. When this solution, concentrated by evaporation, was hydrolysed with strong hydrochloric acid for 2 hours on the water-bath, it yielded, of course, inactive mandelic acid. The substitution of hydroxyl for the maltose radicle, on the other hand, although it proceeds quite rapidly at  $100^{\circ}$ , takes, at the ordinary temperature, a much longer time than the hydrolysis of the nitrile.

Amygdalin (50 grams) was boiled in an open flask with 500 c.c. of the baryta solution until all the ammonia was expelled, the theoretical quantity of oxalic acid was then added to precipitate all the barium, and the filtered solution evaporated to a syrup. When cold, this was dissolved in hydrochloric acid of sp. gr. 1.115, the solution being made up to 250 c.c. with the same solvent. This solution, when examined at intervals in the polarimeter, gave the following results ( $l = 2 \text{ dm.}$ ,  $t = 20^{\circ}$  approximately):

TABLE I.

| Time.    | $\alpha_D$ .    | Time.   | $\alpha_D$ .   |
|----------|-----------------|---------|----------------|
| 0        | $-22.0^{\circ}$ | 4 weeks | $-5.0^{\circ}$ |
| 12 hours | $-21.7$         | 8 "     | $+2.0$         |
| 3 days   | $-20.5$         | 15 "    | $+17.0$        |
| 2 weeks  | $-12.0$         |         |                |

The final reading is not accurate to less than one degree, as the solution had become dark in colour, but it corresponds within the limit of accuracy with the value to be expected from the amount



of dextrose (+15.8°). The mandelic acid produced from amygdalinic acid, even at the ordinary temperature, is therefore also inactive.

The difference in the rates at which amygdalinic acid is produced by dilute baryta solution, and hydrolysed by comparatively strong hydrochloric acid, was very striking, and suggested an examination of the velocity of hydrolysis of amygdalin by hydrochloric acid alone. The following data show clearly the separation of the reaction into two parts, one of which proceeds with a velocity comparable with that due to baryta and is complete after six days. Most probably the first consists also in the transformation of the nitrile radicle into carboxyl, whilst the second—the replacement of the maltose by hydroxyl—goes on very slowly, as indicated in Table I. Ten grams of amygdalin were dissolved in hydrochloric acid (sp. gr. 1.1), the solution being made up to 50 c.c. with the same solvent and filtered rapidly. The observed readings were as follows ( $l = 2$  dm.,  $t = 20^\circ$  approximately):

TABLE II.

| Time.   | $\alpha_D$ . | Change<br>of $\alpha_D$ . | Time.    | $\alpha_D$ . | Change<br>of $\alpha_D$ . |
|---------|--------------|---------------------------|----------|--------------|---------------------------|
| 0       | -13.5°       | —                         | 71 hours | -40.0°       | 26.5°                     |
| 1 hour  | -14.43       | 0.93°                     | 95 "     | -41.3        | 27.8                      |
| 3 hours | -16.12       | 2.62                      | 119 "    | -42.44       | 28.94°                    |
| 6.5 "   | -18.8        | 5.30                      | 143 "    | -42.78       | 29.28°                    |
| 22 "    | -27.5        | 14.00                     | 220 "    | -40.7        |                           |
| 24.5 "  | -28.35       | 14.85                     | 346 "    | -35.8        |                           |
| 47 "    | -35.68       | 22.18                     |          |              |                           |

The change has not yet been followed further, but the final rotation which the solution should show when all the amygdalin has been converted into dextrose and *l*-mandelic acid is easily calculated from the known specific rotations of these two substances. The concentration of the mandelic acid will be 6.28 per cent., its specific rotation, from my own determinations, is about  $-163^\circ$ , and the corresponding values for dextrose are 14.89 per cent. and  $+53^\circ$ . In a 1 dm. tube, the resulting rotation will therefore be  $-10.24^\circ + 7.89^\circ = -2.33^\circ$ . Practically the final rotation was easily reached by warming a portion of the solution for 7 minutes on the water-bath. The liquid became somewhat red in colour, and therefore the observation was not very exact, but it was found to be about  $-2^\circ$ , the value remaining constant after warming in the same way for half an hour longer. After 2 hours' heating, the solution became so dark in colour that polarimetric observations could not be taken, but on treatment with ether it gave a very active ethereal extract, which, on evaporation, left a crystalline solid, easily identified by its melting point as *l*-mandelic acid. A comparison of the values in the above table shows that the first reaction is almost complete in 120 hours, while

the second has proceeded to a very slight extent. One may therefore, with only a small error, take  $30^\circ$  as the total optical change produced in passing from the nitrile to the carboxylic acid, since the rotation of the small amount of mandelic acid formed almost exactly neutralises that of the corresponding amount of dextrose. An almost constant value of  $K$  is obtained on applying to the above values the equation for a unimolecular reaction,  $K = \frac{1}{t} \log_e \frac{A}{A-x}$ , where  $t$  = time in hours.  $A = 30^\circ$ , and  $x = 0.93^\circ$ .

TABLE III.

|         |               |          |               |
|---------|---------------|----------|---------------|
| $t = 1$ | $K = 0.01368$ | $t = 47$ | $K = 0.01242$ |
| 3       | 0.01323       | 71       | 0.01314       |
| 6.5     | 0.01299       | 95       | 0.01194       |
| 22      | 0.01241       | 119      | 0.01220       |
| 24.5    | 0.01211       |          |               |

The results in Table I, which indicate the velocity of the second reaction (the hydrolysis of the maltose radicle), when treated in the same way, also give an approximately constant value 0.0003, so that this change proceeds about 40 times more slowly than the first.

The results indicated in Tables I and II were obtained with solutions of the same concentration with respect to amygdalin. The first table shows that Liebig and Wöhler's amygdalinic acid produced by baryta gives in 20 per cent. solution in the 2 dm. tube an angle of rotation of  $-22^\circ$ , whilst the second shows that the amygdalinic acid produced by hydrochloric acid has a rotation of about  $-42^\circ$  in the same tube, and at the same concentration. Liebig and Wöhler's amygdalinic acid is, therefore, already racemoid with respect to its mandelic asymmetric carbon atom. The results thus far, therefore, pointed to racemisation taking place in the preparation of the amygdalinic acid, that is, during the hydrolysis of the nitrile, since the second stage of the reaction, namely, the substitution of the maltose radicle, is the same in both cases. A reaction of this nature would be sufficiently remarkable to warrant further investigation, because, although instances of racemisation taking place when one of the atoms or groups directly attached to an asymmetric carbon atom is replaced by another atom or group are fairly common when a halogen is the atom undergoing replacement, yet there are but few recorded cases of its occurrence when the atom replaced is not so situated (propoxyphenylacetic acid, McKenzie, Trans., 1899, 75, 764). Another consideration, however, led to the conclusion that racemisation might take place even earlier than this. The specific rotation of amygdalin freshly dissolved in hydrochloric acid solution was

found in the last experiment to be  $-33.75^\circ$ , a value differing but little from that in pure water, whilst in a baryta solution newly prepared and having no odour of ammonia it was found in the first experiment to be about  $-43^\circ$ . The discrepancy between this and the value  $-35.4^\circ$ , found in aqueous solution, might, however, be due to the action of the baryta on one of the hydroxyl groups of the maltose radicle. To settle this point, 10 grams of amygdalin were dissolved in 50 c.c. of the baryta solution. After 10 minutes, and before any odour of ammonia could be detected, 50 c.c. of a dilute sulphuric acid solution, containing the theoretical quantity of  $\text{H}_2\text{SO}_4$  to precipitate all the barium, were added. After settling and filtering, the rotation of the solution at  $20^\circ$  was found to be  $\alpha_D = -4.32^\circ$ ,  $l=1$  dm., hence  $[\alpha]_D^{20} = -43.2^\circ$ . The increased rotation of the amygdalin is therefore not due to the presence of, or to combination with, the baryta, since the specific rotation remains unaltered after the barium has been precipitated. When evaporated down, either on the water-bath or spontaneously, this solution did not crystallise, even after some time, but left a viscous gum. It appears, therefore, that solution in dilute aqueous baryta produces in a very short time, without any appreciable hydrolysis of the nitrile radicle having taken place, a very marked change, not only in the rotatory power, but also in the solubility of amygdalin. In order to determine whether racemisation had already taken place, a similar solution to the last one was prepared and, after 10 minutes, was almost neutralised with hydrochloric acid; it was then evaporated to a syrup which, when cold, was dissolved in hydrochloric acid (sp. gr. 1.1), the volume being made up to 50 c.c. with the same solvent. The rotation of this solution in the 1 dm. tube was  $-10^\circ$ . A portion of the solution, when heated for 10 minutes to  $67^\circ$  only, to avoid darkening in colour, gave a rotation of  $-8.55^\circ$ , and after 10 minutes' additional heating at the same temperature  $+7.25^\circ$ . The rotation due to the dextrose alone if all were hydrolysed would be  $+7.9^\circ$ . The solution was further heated on a boiling water-bath for 10 minutes and, as it had become too dark for examination in the polarimeter, was extracted with ether. The ethereal extract showed only very little activity, and left on evaporation, a crystalline solid, easily identified as *i*-mandelic acid by a determination of its melting point. Racemisation is therefore effected by simple solution in dilute aqueous baryta. A second portion of the solution in aqueous hydrochloric acid was examined in the 2 dm. tube at the room-temperature (about  $20^\circ$ ) at various intervals:



TABLE IV.

| Time.   | $\alpha_D$ . | Change<br>of $\alpha_D$ . | Time.      | $\alpha_D$ . | Change<br>of $\alpha_D$ . |
|---------|--------------|---------------------------|------------|--------------|---------------------------|
| 0       | -20.0°       | —                         | 67 hours   | -20.95°      | -0.95°                    |
| 4 hours | -20.1        | -0.1°                     | 76 „       | -20.91       | -0.91                     |
| 19 „    | -20.85       | -0.85                     | 250 „      | -14.2        | +5.80                     |
| 43 „    | -21.0        | -1.0                      | 296 „      | -13.32       | +6.68                     |
|         |              |                           | $\infty$ „ | +15.8        |                           |

In this case also, as with *l*-amygdalin (Table II), it is evident that the hydrolysis takes place in two stages, and a very strong indication that the new substance is racemoid amygdalin is seen in the general correspondence of the velocities of the two reactions as indicated by the change in rotation. The total change from the most *lævo*- to the most *dextro*-reading is about 37° in both cases, and after 300 hours both have become altered to approximately the same extent, the amount of transformation being 7/37ths of the entire change represented by the second stage. In the case of the racemoid substance, however, the first stage is accompanied by only a very small change in optical power, whilst with *l*-amygdalin the corresponding stage involves a very large change of rotation.

If the racemisation of amygdalin is, as the foregoing observations seem to indicate, a catalytic action induced by the presence of alkalis, a very small quantity of the latter ought to effect the change, although not so rapidly. It might also be brought about in a longer time by the alkaline carbonates. The following experiments confirm this supposition. Amygdalin (10 grams) was placed in a 50 c.c. flask and some water was added. Then 10 c.c. of the baryta solution were run in and the flask was filled to the mark with water. It took 15 minutes' shaking to effect solution, whereas 50 c.c. of the same baryta solution dissolve 10 grams of amygdalin almost instantly. The rotation observed in the 1 dm. tube was -10.15°, and this remained unchanged after 16 hours. Twenty-five c.c. of the solution were then saturated with carbonic acid and filtered. The optical power was almost unchanged, namely, -9.88°. The solution was evaporated to a syrup, the residue being dissolved in hydrochloric acid (sp. gr. 1.1), the final volume of which is made up to 25 c.c. The rotation was now -9.57°, *l*=1 dm., and this remained almost constant for two days, as was found previously for the racemoid substance (see Table IV). A portion of the hydrochloric acid solution was warmed on the water-bath at a temperature of nearly 100° for 10 minutes, when its rotation changed to -4.58°, and after 10 minutes' additional heating to +5°. The mandelic acid

produced was therefore inactive, this final dextro-rotation being due to the dextrose produced. A similar experiment was performed in which only 5 c.c. of the baryta solution were employed for the same weight of amygdalin, and, although the glucoside took a slightly longer time to dissolve, yet the rotation of the resulting solution was the same. In this last experiment, the proportion is only 0.03 mol. of barium hydroxide to 1 mol. of amygdalin, and the effect is the more striking as it causes 10 grams of amygdalin to dissolve in 50 c.c., whereas 120 c.c. of pure water are required for the same weight of the glucoside at the ordinary temperature. A very small quantity of potassium carbonate was also found to induce racemisation. Ten grams of amygdalin were placed in a 50 c.c. flask, which was filled to the mark with a solution containing 0.1886 gram  $K_2CO_3$  in 100 c.c. of water, this being equivalent to using 10 c.c. of the baryta solution. It took two hours' constant shaking to effect solution, and the rotatory power in the dem. tube was almost the same as in the last two experiments, namely,  $\alpha_D = -9.7^\circ$ . The racemisation of amygdalin is apparently, therefore, a catalytic action, depending most probably on the presence of hydroxyl ions in the solution.

That daylight has no effect in inducing the action in the presence of baryta was shown by an experiment similar to one already described, where 10 grams of amygdalin, 50 c.c. of baryta solution, and 50 c.c. of an equivalent sulphuric acid solution were employed. The whole operation was performed in the dark, but in this case also the product was racemoid.

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### LIII.—*Camphor- $\beta$ -thiol.*

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THE readiness with which large quantities of camphorsulphonic acid can be prepared by the well-known Reychler method of sulphonation suggested to us the desirability of making an attempt to reduce the sulphochloride of this acid and so to prepare the hitherto unknown mercaptan of the camphor series, a substance likely to possess interesting pharmacological properties. In this, we have been only partially successful. Camphorthiol is, indeed, produced by this method, but the yield of the mercaptan is always small, never exceeding 15 per cent. of the theoretical quantity, and in spite of many attempts to

effect an improvement by varying the conditions we have been unable to secure a result which will compare in any way with the almost theoretical yields which the method gives when applied to sulphochlorides of the benzene series.

In our earlier experiments, the reduction was carried out by means of zinc dust and hydrochloric acid, but latterly we have found that a larger and very much more regular yield of the thiol is obtained when powdered tin is used in the place of zinc. The method of preparation is as follows: 25 grams of dried and powdered potassium camphor-sulphonate are ground in a mortar with 20 grams of phosphorus pentachloride; the liquid product is allowed to stand for an hour, and is then poured on to ice; the sulphochloride soon solidifies, and, after being well washed and drained on the filter-pump, can be reduced without further purification. In this operation, the sulphochloride is covered with 200 c.c. of concentrated hydrochloric acid, 40 grams of powdered tin are added in small quantities, and the mixture is warmed occasionally to  $50^{\circ}$ . When all the tin has been introduced, the product is allowed to remain for 24 hours. Concentrated hydrochloric acid (20 c.c.) is then added and the flask connected to a condenser and heated on a water-bath. On passing steam into the mixture, the thiol is rapidly carried over and solidifies in the condenser. The product thus obtained is practically pure and can generally be used without recrystallisation. The yield is about 10 per cent. of the weight of the potassium salt taken, or 14 per cent. of the theoretical quantity.

*Camphor- $\beta$ -thiol*,  $\text{HS} \cdot \text{C}_8\text{H}_{13} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , is a colourless solid of character-

istic and not unpleasant odour, faintly recalling with camphor, the odour of burnt india-rubber. It is easily volatile in a current of steam, and can be effectively purified by crystallising from ordinary methylated spirit, from which it separates in small, transparent prisms; less favourable results are obtained when absolute alcohol or light petroleum is used as a solvent. When purified by crystallising once from spirit, the thiol melts at  $66^{\circ}$ , and the melting point is not changed by further crystallisation. The rotatory power was determined in a solution in acetone containing 10 grams per 100 c.c., and was found to be  $[\alpha]_D^{25} = +6^{\circ}$ . On combustion with lead chromate:

0.1773 gave 0.4255  $\text{CO}_2$  and 0.1374  $\text{H}_2\text{O}$ . C = 65.44; H = 8.67.

$\text{C}_{10}\text{H}_{16}\text{OS}$  requires C = 65.14; H = 8.77 per cent.

By slow evaporation of a solution in acetone, the thiol was obtained in well-formed crystals, approximately cubic in shape; these crystals were sometimes very large, the individual crystals weighing nearly a gram; no edge faces were developed, and it was therefore impossible



to determine completely the geometrical constants of the crystals; the optical properties, however, were readily determined, and proved invaluable in allocating the crystals to their proper system. The following results were obtained:

*System.* Orthorhombic.\*

*Axial ratios:*

$$a : b : c = 1.052 : 1 : 1$$

*Forms present:*

$$\begin{aligned} p &= \{110\}. \quad c = \{001\}. \\ c : p \quad 001 : 110 &= 90^{\circ}0'. \\ p : p \quad 110 : 1\bar{1}0 &= 87^{\circ}6'. \\ p : p \quad 110 : \bar{1}10 &= 92^{\circ}55'. \end{aligned}$$

*Optical Properties.*—On examining the supposed "cubes" between crossed Nicols in a parallel beam of polarised light, it was found that on two pairs of faces very sharp extinctions occurred when the plane of polarisation was parallel or perpendicular to the edges of the face; on the third pair of faces, however, the extinctions occurred when the plane of polarisation lay diagonally across the face. This showed that four of the faces must be regarded as constituting a prism form and the remaining two as pinacoids; this view was confirmed by geometrical measurements, which showed that the angles in the prism zone were not right-angles, but had the values  $87^{\circ}6'$  and  $92^{\circ}55'$ , given above. On cutting sections across the acute edge of the prism and examining these in a convergent beam of polarised light, exceptionally brilliant optic axial figures were seen; the plane of the optic axis is perpendicular to the axis of the prism and parallel to the faces of the pinacoid form  $\{001\}$ ; the optic axial angle is fairly large and showed marked dispersion, the angle being greatest for the blue rays; the acute bisectrix was taken as the axis of  $a$ . The double refraction is positive in sign.

The crystallographic properties of the thiol bring it into line with  $\beta$ -bromocamphor, which also crystallises in the orthorhombic system and has  $a : b = 1.062 : 1$ ,  $110 : 1\bar{1}0 = 86^{\circ}32'$ , and  $110 : \bar{1}10 = 93^{\circ}28'$ . The optic axes are differently situated, but the sign of the double refraction is the same in each case. Unlike  $\beta$ -bromocamphor and  $\beta$ -chlorocamphor, the thiol is dimorphous, and two forms are seen successively on allowing it to cool from the melting point on a microscope slide.

The thiol does not form any alkali salts, and is precipitated completely on adding water to an alcoholic solution containing potassium

\* Or possibly monosymmetric, in which case  $\beta = 87^{\circ}6'$  and the axial ratios are indeterminate.

hydroxide. Like other mercaptans, however, it possesses the property of forming stable compounds with lead and mercury.

The insoluble *lead* salt,  $\text{Pb}(\text{SC}_{10}\text{H}_{15}\text{O})_2$ , was prepared by precipitating an alcoholic solution of the thiol with alcoholic lead acetate :

0.4078 gave 0.2160  $\text{PbSO}_4$ .  $\text{Pb} = 36.1$  (calc. 36.0).

By precipitating an alcoholic solution of the thiol with alcoholic mercuric chloride, the *mercurichloride*,  $\text{Cl}\cdot\text{Hg}\cdot\text{S}\cdot\text{C}_{10}\text{H}_{15}\text{O}$ , was produced ; this is insoluble in water, but is very slightly soluble in boiling alcohol, from which it separates on cooling in minute, glistening scales, rendering the liquid opalescent. The chlorine was determined by boiling with silver nitrate and dilute nitric acid ; the hot filtrate deposited a sparingly soluble compound which is perhaps the mercuri-nitrate :

0.6553 gave 0.2144  $\text{AgCl}$ .  $\text{Cl} = 8.08$  (calc., 8.4).

The *disulphide*,  $\text{S}_2(\text{C}_{10}\text{H}_{15}\text{O})_2$ , was prepared by oxidising an alcoholic solution of the thiol by means of ferric chloride and also by the action of iodine. When purified by crystallising from dilute spirit, in which it is somewhat readily soluble, the product in each case melted constantly at  $224^\circ$ . It separates from solution in feathery needles, but could not be obtained in measurable crystals. The specific rotatory power was found to be  $[\alpha]_D^{25} - 97^\circ$  in a solution in acetone containing 2.70 grams per 100 c.c. The formation of the disulphide takes place very readily under a number of different conditions, although it is not always easy to separate it in a pure state. It is formed when an alcoholic solution of the thiol is diluted with ammonia and left exposed to the air, and was also produced on attempting to brominate the acetyl compound described below. A substance which is probably an impure form of the disulphide was also obtained when the liquors from the preparation of the thiol by means of zinc dust and hydrochloric acid were exposed to the air ; after several crystallisations, it melted at about  $200^\circ$  and had  $[\alpha]_D - 50^\circ$  in acetone ; a mixture with the disulphide melted at an intermediate temperature. The formation of this substance appears to us to indicate that the thiol forms a zinc derivative which is not readily decomposed by acids ; this view is confirmed by the fact that a small additional amount of the readily volatile thiol was usually obtained on each addition of acid during steam distillation, even when the whole of the zinc had been dissolved.

The disulphide was also obtained on attempting to prepare the oxime of the thiol ; this is scarcely to be wondered at in view of the fact that alcoholic ammonia brings about a similar change. Two grams of the thiol and 1 gram of hydroxylamine hydrochloride were dissolved in alcohol and a solution of 0.3 gram of sodium in alcohol was added ;

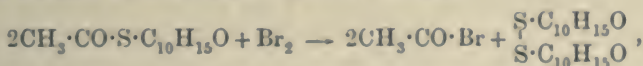
the mixture was boiled for an hour, the precipitated salt was collected, and part of the alcohol evaporated; the solution was then precipitated with water and the product drained and recrystallized three times from dilute alcohol; this substance, which was then found to be free from nitrogen, melted at  $212^\circ$  and had  $[\alpha]_D -100^\circ$ , these values being sufficiently near to those for the disulphide to indicate the nature of the product.

A well-defined *acetate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{S}\cdot\text{C}_{10}\text{H}_{15}\text{O}$ , was prepared by boiling the thiol with sodium acetate and acetic anhydride. On diluting with water, an oil was precipitated from which the acetate gradually separated in long, needle-shaped crystals; minute, colourless needles were also deposited from the aqueous liquor. On account of its low melting point, the acetate could not be purified by crystallising in the ordinary way, but by slow evaporation of an alcoholic solution it was again obtained in long needles melting at  $38^\circ$ ; its readiness to separate in large crystals distinguishes it in a marked way from the preceding compound. The specific rotatory power was found to be  $[\alpha]_D^{25} -41^\circ$  in a solution in alcohol containing 5 grams per 100 c.c. On combustion with lead acetate:

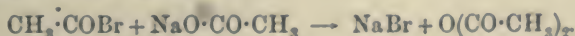
0.1223 gave 0.2842  $\text{CO}_2$  and 0.0894  $\text{H}_2\text{O}$ . C = 63.38; H = 8.18.

$\text{C}_{12}\text{H}_{15}\text{O}_2\text{S}$  requires C = 63.66; H = 8.04 per cent.

It was thought that in the acetate the thiol group would be sufficiently protected to allow of the preparation of a number of derivatives which could not be prepared from the thiol itself. This did not prove to be the case; the acetyl derivative was decomposed almost as readily as the thiol, giving derivatives of the disulphide. With a view to preparing an  $\alpha$ -bromo-derivative, the acetate was dissolved in acetic acid, together with sodium acetate, and bromine was added; the bromine was at once decolorised and sodium bromide separated, but the product was found to be free from bromide and was identified as the disulphide. Probably bromine first combines with the acetyl groups forming a disulphide and acetyl bromide,



and the acetyl bromide in presence of sodium acetate yields sodium bromide and acetic anhydride,



The corresponding *benzoate*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{S}\cdot\text{C}_{10}\text{H}_{15}\text{O}$ , was readily prepared by the Schotten-Baumann method, a little purified ether being added to bring the thiol into solution. The product, after allowing the ether to evaporate, was still soft, but became hard when rubbed



with a glass rod ; it was then drained, washed, and crystallised from spirit. When crystallised a second time from hot spirit, in which it is fairly readily soluble, it separated in pearly scales and melted at  $59^{\circ}$ . The specific rotatory power was found to be  $[\alpha]_D^{13^{\circ}} - 16.4^{\circ}$  in a solution in acetone containing 3.22 grams per 100 c.c.

In conclusion, we wish to express our thanks to Prof. Armstrong for the interest he has taken and the help he has afforded in this investigation.

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#### LIV.—*Hydrolysis of Urea Hydrochloride.*

By JAMES WALKER and JOHN K. WOOD.

It was shown by Walker (*Zeit. physikal. Chem.*, 1889, 4, 321) that very weak bases can be arranged in the order of their strengths by observations of the speed with which equivalent solutions of their hydrochlorides effect the catalysis of methyl acetate, the principle of the method being as follows. The salts of weak bases are partially decomposed in aqueous solution into free acid and free base, the extent of the hydrolysis being greater as the base is feebler. Now the rate at which methyl acetate is converted into methyl alcohol and acetic acid is, other things being equal, roughly proportional to the concentration of the free mineral acid in the aqueous solution. It is therefore possible to measure approximately the extent of the hydrolysis of the hydrochloride of the weak base by comparing the rate at which a given solution of methyl acetate is catalysed under its influence with the rate at which the methyl acetate is catalysed by an equivalent solution of pure hydrochloric acid. Thus Walker found that whilst the rate of catalysis of methyl acetate by normal hydrochloric acid was 0.00315, the rate of catalysis by normal urea hydrochloride under the same conditions was 0.00174. Consequently the value  $0.00174/0.00315 = 0.55$  is obtained as a first approximation to the extent of hydrolysis of urea hydrochloride under the given conditions. In other words a normal solution of urea hydrochloride contains less than half the urea hydrochloride as such, about 55 per cent. of the whole being decomposed by the water into free urea and free hydrochloric acid.

The rate of inversion of cane sugar, which rests on a similar basis, is also available for the same purpose, and was applied by Walker and

Aston (Trans., 1895, 67, 576) to the salts of both organic and inorganic bases.

These methods have since been employed by others, but chiefly with a view to comparing bases with each other rather than to determine accurately the extent of hydrolysis in any one case. The object of the present research is to investigate the conditions under which an exact determination of the hydrolytic dissociation is possible by either method, urea hydrochloride being chosen as a typical example of a salt of a very weak base. For stronger bases such as aniline the more convenient conductivity method (Walker, *loc. cit.* 333; Bredig, *Zeit. physikal. Chem.*, 1894, 13, 321) may be employed with advantage.

### *Mode of Experiment.*

For a description of the method of experiment, reference may be made to Ostwald's *Physico-chemical Measurements*, pp. 250—2, the thermostat employed being of the type figured on p. 59 of that work. We have found that by far the best bearing for the stirring-gear in the thermostat is the head of a common pin working on a concave glass surface such as the end of a test-tube fitted into a weighted cork. The glass tube which forms the axis of the stirring-gear is drawn out to a jet like that of a wash-bottle, and a pin is inserted loosely into the hole so that only the head projects. The stirrer which we used revolved on such a pin for several months without at any time stopping or requiring the slightest attention.

In the experiments on sugar-inversion, the polarimeter was placed alongside the thermostat in order that the observation tube might be heated by water which passed at constant pressure through coils of metal pipe lying under the vanes of the stirrer. The polarimeter read to  $0.01^\circ$ , and the observation tube was 20 cm. in length. We did not find it necessary to use a dark room to obtain accurate readings, the instrument being merely screened from the direct light of the windows. The jacket of the observation tube was blackened, and the Landolt sodium lamp was contained in a blackened box, into which the objective end of the polarimeter projected.

The solutions of urea hydrochloride which we used were in every case prepared by weighing out a certain amount of urea, adding the equivalent quantity of an accurately normal solution of hydrochloric acid and making up to the required bulk. Thus if 50 c.c. of a seminormal solution of urea hydrochloride were wanted, 1.5 grams of urea were dissolved in 25 c.c. of normal hydrochloric acid, and the solution made up to 50 c.c. In the methyl acetate experiments, 20 c.c. of the solution were usually mixed with 1 c.c. of pure methyl acetate; in the sugar inversion experiments, equal volumes of the chloride

solution and the sugar solution were mixed, the mixing in each case taking place after the solutions had reached the experimental temperature.

The formula used in calculating the results was

$$\frac{1}{t} \log. \frac{A}{A-x} = C.$$

$A$  is the difference between the initial and final readings,  $x$  the difference between the initial reading and that at the time  $t$ .  $C$  is then a constant which is roughly proportional to the concentration of the hydrochloric acid in the solution.

The following numbers for one set of experiments by each method will afford an idea of the degree of accuracy in determining the constant.

*N/5 Solution of Urea Hydrochloride.—Methyl Acetate Method.*

| $t$ .    | Burette reading. | $x$ .       | $C$ .         |
|----------|------------------|-------------|---------------|
| 0        | 3.70             | 0           | —             |
| 165      | 7.45             | 3.75        | 0.001245      |
| 195      | 8.00             | 4.30        | 0.001261      |
| 217      | 8.32             | 4.62        | 0.001249      |
| 247      | 8.72             | 5.02        | 0.001235      |
| 367      | 9.02             | 5.32        | 0.001245      |
| $\infty$ | 13.90            | $A = 10.20$ | Mean 0.001247 |

*N/5 Solution of Urea Hydrochloride.—Sugar Inversion Method.*

| $t$ .    | Rotation. | $x$ .      | $C$ .         |
|----------|-----------|------------|---------------|
| 0        | +6.45°    | 0          | —             |
| 95       | 3.15      | 3.30       | 0.002358      |
| 113      | 2.66      | 3.79       | 0.002388      |
| 130      | 2.23      | 4.22       | 0.002419      |
| 151      | 1.93      | 4.52       | 0.002309      |
| 175      | 1.45      | 5.00       | 0.002340      |
| $\infty$ | -1.74     | $A = 8.19$ | Mean 0.002363 |

In the succeeding portions of this paper, every value of  $C$  given is the mean of such a set of determinations.

It has already been stated that the value of the constant  $C$  is only roughly proportional to the amount of free hydrochloric acid present in the solution of the hydrochloride of a weak base. Change in the degree of electrolytic dissociation of the hydrochloric acid and the direct action of the undecomposed hydrochloride on the velocity constant are the chief disturbing factors. The principle of procedure



which we therefore adopted was to make a rough determination of the hydrolysis as above indicated, and then to prepare a solution which should contain hydrochloric acid and neutral chloride in the proportions shown by the preliminary experiment, this solution being then compared directly against the urea solution. For example a preliminary experiment with a seminormal solution of urea hydrochloride at 25° when investigated by the methyl acetate method, showed that the hydrolysis was about 65 per cent. A solution was therefore prepared, which was seminormal with respect to total chloride, but contained 65 per cent. of this as free hydrochloric acid and 35 per cent. as neutral sodium chloride. This solution was then compared directly with a solution of seminormal urea hydrochloride, the same quantity of methyl acetate being added to each. As the rate of catalysis was in both cases nearly the same, any disturbing influence such as a slight fluctuation in the temperature of the thermostat affected both solutions equally at similar stages of the reaction, so that the results obtained are strictly comparable. Under these conditions the value of  $C$  for urea hydrochloride was 0.001081 and for the known solution 0.001021. We conclude therefore that the amount of hydrolysis in the urea hydrochloride solution is  $\frac{65 \times 1081}{1021} = 68.8$  per cent. Since the error in the mean value of  $C$  is under 1 per cent., the hydrolysis value may be taken as having a similar degree of accuracy.

In the above experiment we have neglected the effect of the free urea as affecting the catalytic power of the free hydrochloric acid. This we are justified in doing, since the displacement of small quantities of water in the solution by another non-electrolyte, has been frequently shown to have no effect on the velocity constant of the particular reaction considered.

It might reasonably be objected that the hydrolysis found above is not the value which would be obtained in a pure aqueous solution of urea hydrochloride, since the solution actually considered contained about 4 per cent. by weight of methyl acetate. The following experiments made with seminormal solutions at 35° show that this objection has little weight, for practically the same hydrolysis was found whether 0.5, 1 or 2 c.c. of methyl acetate were added to 20 c.c. of solution.

| Methyl acetate added. | 68 per cent. HCl +<br>32 per cent. NaCl. | Urea hydrochloride. | Hydrolysis. |
|-----------------------|--|---------------------|-------------|
| 0.5 c.c.              | $C = 0.00257$                            | $C = 0.00255$       | 0.675       |
| 1.0 „                 | 249                                      | 249                 | 0.680       |
| 2.0 „                 | 257                                      | 254                 | 0.672       |

It may therefore be safely concluded that the hydrolysis value in

pure aqueous solution will not differ greatly from the value obtained in the actual solution investigated.

When the sugar inversion method was employed, the solutions contained 5 per cent. of cane sugar, but here also the quantity of sugar present has little influence on the extent of hydrolysis, as the following experiments at 35° serve to prove.

| Cane sugar present. | 82 per cent. HCl +<br>18 per cent. NaCl. | Urea hydrochloride. | Hydrolysis. |
|---------------------|--|---------------------|-------------|
| 5 per cent.         | C = 0.00235                              | C = 0.00236         | 0.823       |
| 10     ,,           | 249                                      | 252                 | 0.830       |

*Comparison of the Methods.*

That the methyl acetate and cane sugar methods lead to the same results is apparent from the subjoined tables.

*N/4 solutions at 25°.*

| Method.         | Comparison solution. |       |                |      | Hydrolysis. |
|-----------------|----------------------|-------|----------------|------|-------------|
| Cane sugar..... | 75.6 per cent.       | HCl + | 24.4 per cent. | NaCl | 0.785       |
| ,,       .....  | 78.0                 | ,,    | + 22.0         | ,,   | 0.783       |
| Methyl acetate. | 75.6                 | ,,    | + 24.4         | ,,   | 0.790       |
| Mean.....       |                      |       |                |      | 0.786       |

*N/4 solutions at 35°.*

|                 |              |       |              |      |       |
|-----------------|--------------|-------|--------------|------|-------|
| Cane sugar..... | 79 per cent. | HCl + | 21 per cent. | NaCl | 0.793 |
| Methyl acetate. | ,,           | ,,    | ,,           | ,,   | 0.790 |
| Mean.....       |              |       |              |      | 0.791 |

*N/5 solutions at 35°.*

|                 |              |       |              |      |       |
|-----------------|--------------|-------|--------------|------|-------|
| Cane sugar..... | 82 per cent. | HCl + | 18 per cent. | NaCl | 0.823 |
| Methyl acetate. | ,,           | ,,    | ,,           | ,,   | 0.820 |
| Mean.....       |              |       |              |      | 0.821 |

*N/10 solutions at 35°.*

|                 |                |       |                |     |       |
|-----------------|----------------|-------|----------------|-----|-------|
| Cane sugar..... | 89.5 per cent. | HCl + | 10.5 per cent. | HCl | 0.908 |
| Methyl acetate. | ,,             | ,,    | ,,             | ,,  | 0.902 |
| Mean.....       |                |       |                |     | 0.905 |

So far then as results are concerned, we may choose either method as suits our convenience. The chief advantage of the methyl acetate method is that no expensive apparatus is required. On the other hand it is somewhat less rapid than the cane sugar method, a consideration which may be of importance when experiments are conducted in very dilute solution or at a low temperature.

### *Influence of Temperature.*

A special set of experiments was made by the methyl acetate method in order to ascertain the effect of temperature on the hydrolysis in such a range as would ordinarily be adopted in dealing with weak bases like urea. In general, it has been found that there is a slight increase in the amount of hydrolysis with rise of temperature, the effect depending ultimately on the relative values of the heat of ionisation of the weak base and of water. The results obtained by us for urea were as follows.

| Concentration. | Hydrolysis at 25°. | Hydrolysis at 40°. |
|----------------|--------------------|--------------------|
| N/2            | 0.684              | 0.680              |
| N/4            | 0.792              | 0.801              |
| N/10           | 0.905              | 0.906              |

The numbers obtained agree so closely that we may assume the degree of hydrolysis within the range considered to be practically unaffected by the temperature. This result is in agreement with the experiments of Fawsitt on the decomposition of urea (*Zeit. physikal. Chem.*, 1902, 41, 627).

### *Influence of Dilution.*

It was proved experimentally by Walker (*loc. cit.*, 326) that in normal solutions of hydrochloric acid, to which varying amounts of urea had been added, the hydrolysis equilibrium was governed by the following law:

$$\frac{(\text{Free acid}) \times (\text{Free base})}{(\text{Salt})} = \text{Constant.}$$

The discussion of this case, from the point of view of the ionisation hypothesis, was afterwards given by Arrhenius (*Zeit. physikal. Chem.*, 1890, 5, 16). If we apply the above general law to the case in which the urea and the acid are always present in equivalent proportions, the dilution of the solution alone being subject to variation, we obtain an expression resembling Ostwald's dilution law for binary electro-



lytes. Let  $x$  be the hydrolysed proportion of the salt,  $1 - x$  the unhydrolysed proportion, and  $v$  the volume in which 1 gram-molecule of the salt is dissolved, then we find the hydrolysis to be regulated by the equation:

$$\frac{x^2}{(1-x)v} = k.$$

If we calculate the value of the constant  $k$  from Walker's results in normal solution at  $25^\circ$ , we find it to be  $k = 0.781$ . From this constant we may now, by means of the above equation, calculate the degree of hydrolysis  $x$  for the dilutions employed by us and compare the numbers obtained with the direct results of our experiments. The comparison is given in the following table:

| $v$ . | $x$ calc. | $x$ found (I). | $x$ found (II). |
|-------|-----------|----------------|-----------------|
| 2     | 0.693     | 0.684          | 0.684           |
| 4     | 0.797     | 0.792          | 0.791           |
| 5     | 0.826     | 0.820          | —               |
| 10    | 0.897     | 0.905          | 0.893           |

The agreement between the second and third columns is as satisfactory as could be expected. The values in the fourth column were obtained in solutions which, although having the concentration given by the first column with respect to urea hydrochloride, were all made seminormal with respect to total chloride by the addition of an appropriate amount of sodium chloride; an equal amount of sodium chloride was of course added to the comparison solution. In this set of experiments therefore the amount of highly ionised electrolyte present was the same at all dilutions. The effect of the addition of the electrolyte is small, but quite perceptible at the highest dilution, and, on the whole, the results are slightly more concordant with the calculated values. Similar experiments were made at  $40^\circ$  and again the same slight lowering of the hydrolysis by the addition of sodium chloride was observed.

| $v$ . | Without sodium chloride. | With chloride up to $N/2$ . |
|-------|--------------------------|-----------------------------|
| 4     | 0.801                    | 0.794                       |
| 10    | 0.906                    | 0.900                       |

A similar reduction of the degree of hydrolysis by the addition of sodium chloride was obtained both at  $25^\circ$  and  $40^\circ$  when acetoxime was substituted for urea as base.

Adopting the value 0.781 as the value of the hydrolysis constant for urea hydrochloride, we obtain at  $25^\circ$  the value  $1.5 \times 10^{-14}$  as the dissociation constant of urea (compare van't Hoff, *Lectures*, Vol. I., 132).

*Summary.*

A comparison method is described which permits the hydrolysis of a salt such as urea hydrochloride to be determined by the catalysis of cane sugar or of methyl acetate with an error not exceeding one per cent.

The results obtained with cane sugar and with methyl acetate are identical.

Within the range of 25—40°, temperature has practically no influence on the hydrolysis of urea hydrochloride.

The influence of dilution on the hydrolysis of urea hydrochloride is expressed by the relation  $\frac{x^2}{(1-x)v} = \text{constant}$ .

The addition of sodium chloride very slightly diminishes the degree of hydrolysis.

The dissociation constant of urea calculated from the hydrolytic experiments is  $1.5 \times 10^{-14}$  at 25°.

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LV.—*Decomposition of Mercurous Nitrite by Heat.*

By PRAFULLA CHANDRA RÂY and JATINDRA NÂTH SEN, M.A., Government of Bengal Research Scholar, Presidency College, Calcutta.

WHEN describing mercurous nitrite in 1896, one of us ventured to express the hope that this salt would prove to be the analogue of silver nitrite in all essential properties (*Zeit. anorg. Chem.*, 1896, 12, 365), and has since shown that, by interaction with ethyl iodide, the substance yields both ethyl nitrite and nitroethane, and that in this production of nitroethane much nitric oxide is evolved (*Annalen*, 1901, 316, 250). A study of the action of heat on mercurous nitrite has emphasised the likeness between this compound and the silver salt.

The mercurous nitrite, in a thin layer, was heated in *vacuo* in a tube connected with a Sprengel pump. In the first experiment, a portion of the tube was blown into a bulb, which was kept immersed in a freezing mixture in order to liquefy, if possible, the nitric oxide evolved; but as none of the gas could be thus condensed, the bulb was discarded in subsequent experiments. The tube was generally heated by means of a Bunsen burner, but sometimes by a spirit lamp, keeping the flame rather low. Care was taken to localise the heating to the lower side of the tube and to just that part of it on which

the nitrite rested, but no attempt was made to carry out the decomposition at a fixed temperature throughout. Heating for nearly two hours at  $195^{\circ}$  failed to decompose the salt completely. The temperature of decomposition in our experiments was probably about  $250^{\circ}$ .

The decomposition was complete in about two minutes. Almost from the outset it was noticed that colourless needles of mercurous nitrate began to shoot out from the upper wall of the tube somewhat away from its heated part, and also that a thin layer of yellow basic nitrate,\* intermixed with minute globules of mercury, was deposited at the sides. The residue, consisting of mercuric oxide, was dull red whilst hot, but on cooling became orange-coloured. It is generally stated that mercuric oxide prepared by dry methods, either by direct oxidation of the metal or by heating mercurous nitrate, is red and crystalline, but the variety here obtained was an orange-coloured, amorphous, impalpable powder, resembling more the precipitated oxide, and therefore containing possibly a trace of basic nitrate. Scarcely any nitrous fumes were noticed until the later stages of the heating, when a faint reddish-brown colour could be seen; the indisputable proof of the evolution of some nitrogen peroxide lay, however, in the soiling of the mercury in the pump. The gas, which was collected and measured, consisted of pure nitric oxide almost completely absorbed by a concentrated solution of ferrous sulphate.

Mercurous nitrite contains 5.70 per cent. of nitrogen, of which, in different experiments, 3.65, 3.20, 3.70, 3.05, 2.93, and 4.21 per cent. were obtained as nitric oxide. In the experiment which gave the last quantity, the tube had been more strongly heated, and most of the nitrate was thereby decomposed. Omitting this one, the mean of the other numbers is 3.31. In the omitted experiment and in the one which gave 2.93 per cent. of nitrogen as nitric oxide, the nitrogen as nitrate in the residue was determined by the Dumas method. In the former case, it was 0.77 per cent., and in the latter 2.23 per cent. The production of nitric oxide equivalent to 3.26 per cent. as nitric oxide and 2.44 per cent. as nitrate—values sufficiently near to 3.31 and 2.23, the numbers found—requires the following equation:  $7(\text{HgNO}_2)_2 = 8\text{NO} + 3(\text{HgNO}_3)_2 + 2\text{HgO} + 6\text{Hg}$ . Allowance for the small quantities of mercuric nitrate and of nitrogen peroxide also produced could, if they were known, be made in this equation without affecting its general character. As for the former compound, its ascertained proportion, together with its equivalent of mercury, would then take the place of the corresponding quantity of mercurous nitrate. The escaping nitrogen peroxide gives rise to mercurous nitrate, which is lost in the

\* The composition of this basic mercurous nitrate will be discussed in a forthcoming paper on mercurous-mercuric nitrates.



pump, and to nitric oxide, which passes through with the rest of this gas directly produced in the decomposition. For example, the difference between 5.7, the total nitrogen, and the sum of 3.31 and 2.23, found as nitric oxide and nitrate, is 0.16, which is nearly 0.4 in  $7(\text{HgNO}_2)_2$ . Taking this to have been lost as  $\text{NO}_2$  in the mercury of the pump, the above equation becomes  $7(\text{HgNO}_2)_2 = 7.6\text{NO} + 0.4\text{N}_2\text{O}_4 + 2.8(\text{HgNO}_3)_2 + 2\text{HgO} + 6.4\text{Hg}$ .

Repeated attempts were made to determine directly the proportions of the components of the heterogeneous residue in the tube, but without success in obtaining results consistent either with the compounds which could be seen on inspection or with the amount of nitric oxide measured. The method consisted in gently shaking the contents of the tube with cold dilute nitric acid (sp. gr. 1.100). A clear solution was quickly obtained, some globules of mercury only being left. The mercurous and mercuric radicles in the solution were estimated in the usual way, whilst the undissolved mercury was not weighed, but its quantity calculated by difference. The method evidently failed in consequence of much of the mercuric oxide and mercury going together into solution as mercurous salt, in spite of the efforts made to prevent this happening.

It will be seen that the results of heating mercurous nitrite serve to confirm those obtained by Divers and Shimidzu with silver nitrite (Trans., 1885, 47, 634). These chemists have shown that silver nitrite is not directly converted into nitrate through oxidation by the nitrogen peroxide, but indirectly from the reduced metal acting on the gas. Silver, however, being non-volatile, they had to perform other experiments in order to prove the point. In our case, such control experiments have been unnecessary, because of the volatility of mercury. Its vapour, acting upon that of the peroxide when both are set free from the nitrite, forms mercurous nitrate, which is deposited on the tube in the manner described, only a small fraction of the mercury remaining in the free state. The decomposition of the salt would seem, then, to proceed in the following manner:  $(\text{HgNO}_2)_2 = 2\text{Hg} + (\text{NO}_2)_2$ , being followed by a secondary reaction \*  $2(\text{NO})\text{NO}_2 + 2\text{Hg} = (\text{HgNO}_3)_2 + 2\text{NO}$ , almost simultaneously set up, as already shown by Divers and Shimidzu.

When the non-oxylic constitution of mercurous nitrite is adopted, the formation of the mercuric oxide has to be explained as being

\* Ramsay and Cundall found that when a mixture of nitric oxide and nitrogen peroxide is kept over mercury, the volume of the gases remains constant, and that the metal is not apparently attacked (Trans., 1885, 47, 191), and think it probable that the care which was taken in drying the product was the cause of the mercury remaining unattacked. We are also of opinion that it is the presence of traces of moisture which brings about the reaction.

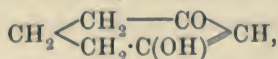
due either to the oxidation of the metal by the nitrogen peroxide  $\text{Hg} + \text{NO}_2 = \text{HgO} + \text{NO}$ , or to the decomposition of the nitrate,  $\text{HgNO}_3 = \text{HgO} + \text{NO}_2$ . The oxide was, however, formed in the tube just where the nitrite lay at the beginning of the experiment, and care was always taken during the heating not to disturb the nitrate on the upper side of the tube. Hence, another explanation seems to be required. The one that occurs to us is that, under the influence of heat, the atoms in some of the molecules of the nitrite arrange themselves as  $\text{Hg}\cdot\text{NO}_2$ , the non-oxylic form, and in others assume the oxylic form,  $\text{HgO}\cdot\text{NO}$ , scission taking place in each case at the indicated point. The decomposition of the salt seems, then, to proceed simultaneously in both directions,\* unless conditions favourable to one mode of decomposition causes this to predominate over the other. Thus the thinness of the layer of the salt, and the degree of suddenness in imparting heat are both operative in modifying the result.

This view of the constitution of mercurous nitrite is also quite in keeping with the fact that it gives rise to both nitroethane and ethyl nitrite. In the case of silver nitrite, we have no means of either proving or disproving this view. The silver oxide, supposing it to be formed, would at once break up into metallic silver and free oxygen, and the latter would then combine with the nitric oxide to form the peroxide. Thus, as far as silver nitrite is concerned, it would make no difference whether we accept the oxylic or non-oxylic constitution of the salt, or both. Fortunately, owing to the stability of mercuric oxide at the temperatures at which we conducted the experiments,† the heating of mercurous nitrite affords evidence that both views are correct.

## LVI.—*Action of Phosphorus Haloids on Dihydroresorcins. Part II. Dihydroresorcin.*

By ARTHUR WILLIAM CROSSLEY and PAUL HAAS.

IN so far as their action has been studied, the phosphorus haloids react with dihydroresorcin, as if it possessed the following formula :



in fact, in an exactly similar way to that already described in the case of dimethyldihydroresorcin (this vol., 110). There is, however,

\* Compare "A Study of the Dynamic Isomerism of Thiourea and Ammonium Thiocyanate" (Reynolds and Werner, this vol., p. 1).

† This we have proved by a blank experiment.

one very noticeable difference between the behaviour of dihydroresorcin and that of its dimethyl derivative, for whereas the latter is quite stable in air, the former can only be kept for a limited time without undergoing decomposition, and its derivatives decompose, for the most part, within a few hours of their production.

With phosphorus trichloride, dihydroresorcin gives rise to 5-chloro-3-keto- $\Delta^4$ -tetrahydrobenzene,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2\text{-CO} \\ \text{CH}_2\cdot\text{CCl} \end{smallmatrix} \text{CH}$ , from which a semicarbazone can be readily prepared, and as on oxidation it yields nothing but glutaric acid, it must possess the above formula.

Phosphorus tribromide leads to the formation of the corresponding 5-bromo-3-keto- $\Delta^4$ -tetrahydrobenzene.

Dihydroresorcin is very vigorously acted on by phosphorus pentachloride and is converted into 3:5-dichloro- $\Delta^{2:4}$ -dihydrobenzene,  $\text{CH} \begin{smallmatrix} \text{CH}=\text{CCl} \\ \text{CH}_2\cdot\text{CCl} \end{smallmatrix} \text{CH}$ , a substance which decomposes with unusual rapidity, and which, on this account, could not be obtained analytically pure. There can, however, be no doubt as to the constitution of this substance, for on solution in glacial acetic acid saturated with hydrogen chloride it is completely reconverted into dihydroresorcin or its hydrochloride, and on oxidation with potassium permanganate, gives rise to succinic acid (compare Trans., 1902, 81, 821):



The oxidation takes place very readily in the cold, and is a far-reaching one, as the majority of the dichloride appears to be converted into carbon dioxide and water, whereas in the case of dichlorodimethyldihydrobenzene (*ibid.*, p. 830) potassium permanganate acts only very slowly in the cold, and when the solution is boiled a good yield of the oxidation products is obtained. The oxidation of chloro- and bromo-ketotetrahydrobenzenes is also much more vigorous than with the corresponding derivatives of dimethyldihydroresorcin.

It has been shown that when dichlorodimethyldihydrobenzene is acted on with excess of phosphorus pentachloride (Trans., 1902, 81, 1536) it is converted into 3:5-dichloro-*o*-xylene, and dichlorodihydrobenzene undergoes a similar change, giving rise to 3:5-dichlorobenzene:



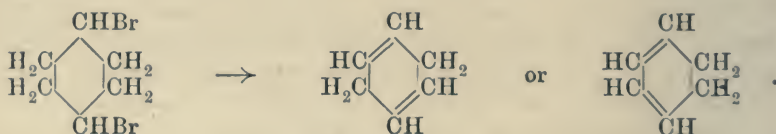
This conversion of a hydroaromatic compound into an aromatic substance is also readily brought about by bromine; for if dichlorodihydrobenzene be dissolved in dry chloroform and a solution of bromine in chloroform added, the latter is rapidly decolorised. On evaporating



off the chloroform and distilling the residue, hydrogen bromide is evolved, and the resulting liquid consists for the most part of *m*-dichlorobenzene, as was proved both by analysis and by the production of its mono- and dinitro-derivatives melting at 33° and 102° respectively (compare Körner, *Jahresber.*, 1875, 323).

This research was originally undertaken with the view of preparing the corresponding hydrocarbon from dichlorodihydrobenzene.

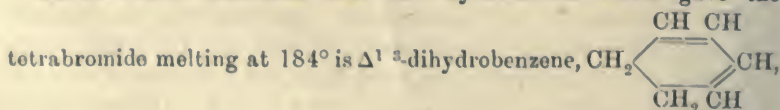
Baeyer was the first to prepare dihydrobenzene by eliminating two molecules of hydrogen bromide from 1:4-dibromohexahydrobenzene by the action of quinoline (*Annalen*, 1894, 278, 94), and thus obtained a liquid boiling at 84—86°, which gave a reddish-violet coloration with alcoholic sulphuric acid, and which on treatment with bromine in chloroform solution was converted into a tetrabromide melting at 184—185° (*ibid.*, p. 96). As Baeyer points out (*ibid.*, p. 113), there are two possible formulæ for a hydrocarbon produced in this manner:



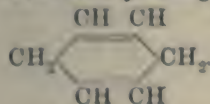
Markownikoff (*Annalen*, 1898, 302, 33) has since expressed the belief that Baeyer's hydrocarbon was a mixture of the two isomerides, because by fractional crystallisation of the tetrabromide he obtained substances of not quite constant melting point.

Markownikoff also treated dichlorohexahydrobenzene with quinoline, and thus prepared, from separate fractions of the dichloro-derivative, hydrocarbons with different properties. Thus from the fraction 190—192° he obtained a hydrocarbon boiling at 83—86° which gave with alcoholic sulphuric acid a raspberry-red coloration, and on treatment with bromine furnished a crystalline tetrabromide melting at 184°; whereas from the fraction 196—198° there resulted a hydrocarbon boiling at 83—86°, developing a dark bluish-violet coloration with alcoholic sulphuric acid and yielding principally an oily tetrabromide from which small quantities of the solid melting at 184° separated. The hydrocarbon obtained from the fraction 194—196° gave a liquid bromide, which deposited crystals melting at 108° and decomposing at 170°, probably identical with the dibromodihydrobenzene described on page 504.

Markownikoff concludes that the hydrocarbon which gave the



and that yielding the liquid tetrabromide is  $\Delta^{1,4}$ -dihydrobenzene

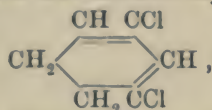


It has been recently shown (Trans., 1902, 81, 832) that the dimethyldihydrobenzene obtained by replacing the two chlorine atoms in dichlorodimethyldihydrobenzene by hydrogen is really 1:1-di-

methyl- $\Delta^{2,4}$ -dihydrobenzene,  $\text{CMe}_2 \begin{array}{c} \text{CH} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{CH} \end{array}$ . The position of the

double bonds in this compound is that which has been dealt with by Thiele (*Annalen*, 1899, 306, 87) in his theory of partial saturation; and this hydrocarbon is characterised by the fact that it only absorbs two atoms of bromine or one molecule of hydrogen bromide, the substance obtained in the latter case being 5-bromo-1:1-dimethyl- $\Delta^3$ -tetrahydrobenzene,  $\text{CMe}_2 \begin{array}{c} \text{CH}_2 - \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CHBr} \end{array} \text{CH}$  (Trans., 1902, 81, 825).

It was therefore expected that dichlorodihydrobenzene,



would give rise to a hydrocarbon exhibiting similar properties, and such proves to be the case.

Unfortunately, the hydrocarbon obtained by treating dichlorodihydrobenzene with sodium in moist ethereal solution is not homogeneous, for the reaction does not cease with the replacement of chlorine by hydrogen, but the resulting dihydrobenzene is further acted on, being partially converted into tetrahydrobenzene, and probably some hexahydrobenzene is also produced.

On oxidation, adipic and succinic acids result; the latter from the oxidation of dihydrobenzene,



and the former from the tetra- or hexa-hydrobenzene.

The mixture of hydrocarbons gives a reddish-violet coloration with alcoholic sulphuric acid, and a nitrosochloride, which, although repeatedly recrystallised from methyl alcohol, had a constant melting point,  $142^\circ$ , whereas the nitrosochloride of tetrahydrobenzene melts at  $152$ — $153^\circ$  (Baeyer, *Annalen*, 1894, 278, 109). Owing, however, to the small amount of material obtained, it was impossible to decide whether this substance was a mixture or not.

When the mixture of hydrocarbons is treated with bromine in chloroform solution, only two atoms are absorbed. In two experiments with different preparations, 138.6 and 134.5 (calc. 160) were obtained for the bromine absorption, the lowness of the results being probably due to the presence of some hexahydrobenzene.

It is important to notice, however, that there was no substance present which absorbed more than two atoms of bromine, nor was any trace of dihydrobenzene tetrabromide (m. p. 184°) obtained on evaporating off the chloroform; \* but transparent crystals melting at 104.5° separated, and these on analysis gave numbers agreeing with the formula  $C_6H_8Br_2$ . It seems, therefore, most probable that this substance is the dibromide of  $\Delta^{1:3}$ -dihydrobenzene:



It is certainly not an aromatic compound, for it decomposes with evolution of hydrogen bromide slowly in air, more readily *in vacuo* or on heating at 170°, and in the latter case a vapour is given off which burns with a smoky flame; moreover, it is slowly attacked by potassium permanganate in the cold and readily on warming.

If further experiments support these conclusions, then the hydrocarbon produced by the above method from dichlorodihydrobenzene is  $\Delta^{1:3}$ -dihydrobenzene,  $CH_2 \begin{array}{c} \diagup CH=CH \diagdown \\ \diagdown CH_2 \cdot CH \diagup \end{array} CH$ , and the hydrocarbon, which gives a solid tetrabromide melting at 184° would be the  $\Delta^{1:4}$ -dihydrobenzene,  $CH \begin{array}{c} \diagup CH \cdot CH_2 \diagdown \\ \diagdown CH_2 \cdot CH \diagup \end{array} CH$ .

The authors are at present conducting a series of experiments on the action of reducing agents on dichlorodihydrobenzene and other similarly constituted compounds, in the hope that the information so acquired will afford a method for preparing the pure dihydrobenzene when the whole question will be more fully investigated.

## EXPERIMENTAL.

### *Phosphorus Trichloride and Dihydroresorcin.*

Twenty grams of dihydroresorcin (3 mols.), prepared according to directions given by Merling (*Annalen*, 1894, 278, 20), were dissolved in 80 grams of dry chloroform, 8.2 grams of phosphorus trichloride (1 mol.) added, and the whole heated on a water-bath for 2 hours, during which time a considerable quantity of hydrogen chloride was

\* The dibromide of tetrahydrobenzene is a liquid boiling at 215–220° under 713 mm. pressure with only slight decomposition (Baeyer, *Annalen*, 1894, 278, 108).



evolved. The liquid product of reaction was poured into ice-cold water, extracted with ether, the ethereal solution washed with aqueous sodium hydroxide and then with water, carefully dried over calcium chloride, and the ether and chloroform distilled off, a method of procedure which was also adopted in other similar preparations described in this communication.

The residue was then purified by distillation under diminished pressure and the chlorine determined :

0.2183 gave 0.2418 AgCl. Cl = 27.44.

$C_6H_7OCl$  requires Cl = 27.20 per cent.

5-Chloro-3 keto- $\Delta^4$ -tetrahydrobenzene,  $CH_2 \begin{array}{c} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{CCl} \end{array} CH$ , is a colourless, highly refractive liquid boiling at  $104^\circ$  (24 mm.), and possesses a somewhat camphorous odour. It slowly turns yellow, decomposes, and deposits crystals, which were washed by decantation with cold acetone, dried on porous plate and then in a vacuum, when they melted at  $130-135^\circ$  with evolution of gas, and gave the following figures on analysis :

0.2084 gave 0.1972 AgCl. Cl = 23.41.

$C_6H_9O_2Cl$  requires Cl = 23.90 per cent.

This substance was in every way identical with *dihydroresorcin hydrochloride*, made for comparison by dissolving some dihydroresorcin in glacial acetic acid saturated with hydrogen chloride, when clusters of prismatic needles slowly separated from the mixture. After purification in the manner described, the crystals softened at  $125^\circ$  and melted with evolution of gas at  $130-135^\circ$ . The hydrochloride is a very unstable substance, deliquescing rapidly on exposure to air, though it may be kept for some time over sulphuric acid in a vacuum. It is insoluble in benzene and cold acetone, very readily soluble in cold water, but can only be obtained crystalline by the method just indicated. On solution in any solvent, it is at once decomposed into dihydroresorcin and hydrochloric acid, as was proved by dissolving a few of the crystals in cold water and adding formaldehyde to the solution, when methylenebisdihydroresorcin melting at  $132-133^\circ$  was obtained (compare Vorländer, *Annalen*, 1899, 309, 356). So completely and rapidly does this decomposition take place, that the chlorine may be estimated by adding silver nitrate to the solution of the hydrochloride in cold water :

0.2198 gave 0.2130 AgCl. Cl = 23.97.

$C_6H_9O_2Cl$  requires Cl = 23.90 per cent.

The chloro-ketone is readily reconverted into dihydroresorcin by solution in glacial acetic acid saturated with hydrogen chloride.

The *semicarbazone*, which separates almost immediately on adding the requisite quantities of semicarbazide hydrochloride and potassium acetate dissolved in water to an alcoholic solution of the ketone, is insoluble in light petroleum, soluble in boiling water or in cold alcohol, chloroform, or acetone, and crystallises from dilute alcohol in glistening flakes melting at  $190^{\circ}$ :

0.1609 gave 30.6 c.c. moist nitrogen at  $11^{\circ}$  and 758 mm.  $N = 22.61$ .

$C_7H_{10}ON_3Cl$  requires  $N = 22.40$  per cent.

*Oxidation of Chloroketotetrahydrobenzene*.—Thirteen grams of the ketone were suspended in 150 c.c. of water and a cold, saturated solution of potassium permanganate added until the colour of the latter remained permanent. After filtering from the separated manganese dioxide, the liquid was evaporated to a small bulk, acidified with sulphuric acid, and repeatedly extracted with ether, when 3.5 grams of a solid were obtained, which, after crystallisation from chloroform melted at  $96-96.5^{\circ}$ :

0.1320 gave 0.2204  $CO_2$  and 0.0771  $H_2O$ .  $C = 45.53$ ;  $H = 6.48$ .

$C_5H_8O_4$  requires  $C = 45.45$ ;  $H = 6.06$  per cent.

This substance was further identified with glutaric acid, by conversion into the anhydride, which separated from ether in long, glistening needles melting at  $76^{\circ}$ .

#### *Phosphorus Tribromide and Dihydroresorcin.*

Twenty grams of dihydroresorcin (3 mols.), 80 grams of dry chloroform, and 16 grams of phosphorus tribromide (1 mol.) were used in this experiment, which was carried out exactly as described on page 499.

The resulting liquid was found to distil constantly at  $132.5-133^{\circ}$ , under 52 mm. pressure:

0.1290 gave 0.1395 AgBr.  $Br = 46.02$ .

$C_6H_7OBr$  requires  $Br = 45.71$  per cent.

5-Bromo-3-keto- $\Delta^4$ -tetrahydrobenzene,  $CH_2 \begin{matrix} \diagup CH_2-CO \\ \diagdown CH_2 \cdot CBr \end{matrix} CH$ , is a pale yellow, highly refractive liquid with a somewhat tarry odour. It rapidly decomposes, depositing crystals of *dihydroresorcin hydrobromide*:

0.1224 gave 0.1191 AgBr.  $Br = 41.40$ .

$C_6H_9O_2Br$  requires  $Br = 41.45$  per cent.

A specimen of the hydrobromide was prepared by dissolving dihydroresorcin in glacial acetic acid saturated with hydrogen

bromide; the crystals which gradually separated were washed with light petroleum, dried in a vacuum, and analysed:

0.1321 gave 0.1267 AgBr. Br = 40.81.

$C_6H_9O_2Br$  requires Br = 41.45 per cent.

The hydrobromide is insoluble in light petroleum, readily soluble in cold acetone, glacial acetic acid, or water, and is an extremely deliquescent substance. When heated in a capillary, it softens at  $134^\circ$  and melts with evolution of gas at  $143\text{--}145^\circ$ .

The *semicarbazone* of bromoketotetrahydrobenzene crystallises from alcohol in silken needles; it melts and decomposes, according to the rate at which it is heated, at temperatures ranging from  $180\text{--}198^\circ$ ;

0.1293 gave 20 c.c. moist nitrogen at  $20^\circ$  and 762 mm. N = 17.73.

$C_7H_{10}ON_3Br$  requires N = 18.10 per cent.

On oxidation with potassium permanganate, the bromo-ketone yields glutaric acid melting at  $96.5^\circ$ , which was further characterised by conversion into its anhydride melting at  $56^\circ$ .

### *Phosphorus Pentachloride and Dihydroresorcin.*

Dihydroresorcin (100 grams), phosphorus pentachloride (280 grams), and dry chloroform (400 grams) were used. As the reaction is liable to become violent, it is necessary to add the pentachloride in small portions at first, and when the addition is complete the heating is only continued until all the pentachloride has gone into solution (10—15 minutes). The liquid was worked up as described on page 499; but although repeatedly distilled *in vacuo*, an analytically pure product (yield 60 per cent. of the calculated amount) could not be obtained, owing to the ease with which the substance decomposes:

0.1188 gave 0.2078  $CO_2$  and 0.0458  $H_2O$ . C = 48.44; H = 4.28.

0.2136 „ 0.3940 AgCl. Cl = 45.63.

0.2146 „ 0.3941 AgCl. Cl = 45.40.

$C_6H_6Cl_2$  requires C = 48.32; H = 4.03; Cl = 47.65 per cent.

3:5-Dichloro- $\Delta^{2:4}$ -dihydrobenzene,  $CH_2 \begin{matrix} \diagup CH=CCl \\ \diagdown CH_2 \cdot CCl \end{matrix} CH$ , is, when freshly distilled, a colourless, highly refractive liquid boiling at  $88\text{--}90^\circ$  under 29 mm. pressure, and possessing an odour resembling that of bitter almonds; it is extremely unstable, rapidly turning yellow and evolving hydrogen chloride, so that it cannot be kept even for a few hours. It readily decolorises a solution of bromine in chloroform, and torrents of hydrogen bromide are evolved (see page 502). When dissolved in glacial acetic acid saturated with hydrogen chloride, clusters of prismatic needles slowly separated,



melting, with evolution of gas, at 130—134°. These consisted of the hydrochloride of dihydroresorcin (see page 499), as was further proved by dissolving them in water and adding formaldehyde to the solution, when methylenebisdihydroresorcin separated, melting at 132—133°.

*Oxidation of Dichlorodihydrobenzene.*—Eleven grams of the dichloride were suspended in 150 c.c. of water, and a cold saturated solution of potassium permanganate added until the colour of the latter became permanent. The solution was then filtered from manganese dioxide, evaporated to a small bulk, acidified with dilute nitric acid, and repeatedly extracted with ether. On evaporating off the solvent, only 0.9 gram of residue remained; this was dissolved in water, the solution decolorised by boiling with animal charcoal, filtered, and cautiously treated with concentrated nitric acid, when transparent, prismatic crystals separated, which melted at 183°, and, as analysis showed, consisted of succinic acid:

0.1225 gave 0.1808 CO<sub>2</sub> and 0.0596 H<sub>2</sub>O. C = 40.25; H = 5.40.

C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> requires C = 40.68; H = 5.08 per cent.

*Conversion of 3:5-Dichloro-Δ<sup>2:4</sup>-dihydrobenzene into m-Dichlorobenzene.*

Ten grams of freshly-prepared dichlorodihydrobenzene were dissolved in 40 grams of dry chloroform, 28 grams of phosphorus pentachloride added, and the whole heated to boiling for 6 hours, during which time hydrogen chloride was slowly evolved. The solution was worked up in the usual way, and the residue distilled in air, when the whole boiled between 170° and 180°, and, on rectification, between 170° and 172° (*m*-dichlorobenzene, b. p. 172°):

0.1515 gave 0.2990 AgCl. Cl = 48.77.

C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> requires Cl = 48.30 per cent.

In order to further establish the identity of this liquid with *m*-dichlorobenzene, it was converted into 1:3-dichloro-4-nitrobenzene (m. p. 32°, see Körner, *loc. cit.*), by treating with fuming nitric acid. The nitro-compound, which crystallised from alcohol in yellow, silken needles, melted at 33—34°. The liquid also yielded 1:3-dichloro-4:6-dinitrobenzene (*ibid.*), by the action of a mixture of fuming nitric and sulphuric acids, the product crystallising from a mixture of alcohol and ether in canary-yellow, flattened needles melting at 102°.

0.2290 gave 23.2 c.c. moist nitrogen at 17° and 757 mm. N = 11.71.

C<sub>6</sub>H<sub>2</sub>O<sub>4</sub>N<sub>2</sub>Cl<sub>2</sub> requires N = 11.81 per cent.

The conversion of the aromatic dichloride into *m*-dichlorobenzene can also be brought about by the action of bromine, for on dissolving the dichloride in chloroform and adding bromine, the latter is rapidly

absorbed and hydrogen bromide eliminated. After evaporating off the chloroform, the residual liquid distilled for the most part between  $171^{\circ}$  and  $173^{\circ}$ , and gave the above-mentioned mono- and dinitro-derivatives, melting respectively at  $32^{\circ}$  and  $102^{\circ}$ .

*Reduction of Dichlorodihydrobenzene.*

Dichlorodihydrobenzene (110 grams) was treated in quantities of 15 grams at a time with sodium in moist ethereal solution, in a manner exactly analogous to that employed in the preparation of dimethyldihydrobenzene (Trans., 1902, 81, 832). The resulting liquid, which boiled between  $70^{\circ}$  and  $90^{\circ}$ , was twice distilled over metallic sodium, when the following fractions were collected: (i) below  $78^{\circ}$  = 1 gram; (ii)  $78-80^{\circ}$  = 3 grams; (iii)  $80-83^{\circ}$  = 26 grams.

The fraction  $80-83^{\circ}$  was again distilled over sodium, when it boiled constantly at  $81-82^{\circ}$  under 755 mm. pressure, and was analysed, with the following results:

0.0984 gave 0.3206  $\text{CO}_2$ , and 0.0983  $\text{H}_2\text{O}$ . C = 88.86; H = 11.09.

0.1026 „ 0.3352  $\text{CO}_2$ , „ 0.1022  $\text{H}_2\text{O}$ . C = 89.10; H = 11.07.

$\text{C}_6\text{H}_8$  requires C = 90.00; H = 10.00 per cent.

$\text{C}_6\text{H}_{10}$  „ C = 87.88; H = 12.20 „

Dr. Perkin, sen., kindly examined this liquid, and reported that its magnetic rotation was 7.385, that of tetrahydrobenzene is 6.392, and dihydrobenzene should be about 8.99. The sp. gr. was 0.8261 at  $15^{\circ}/15^{\circ}$ , whereas dihydrobenzene has a sp. gr. 0.8498, and tetrahydrobenzene 0.8034, both at  $15^{\circ}/15^{\circ}$ .

Unfortunately, as these data show, this substance is a mixture of di- and tetrahydrobenzenes, and probably also contains some hexahydrobenzene, as is suggested by the bromine absorption numbers. It is a colourless, highly refractive liquid, with an odour resembling that of leeks, develops with concentrated sulphuric acid in alcoholic solution an intense reddish-violet coloration (compare Baeyer, *Annalen*, 1894, 278, 94), and resinifies on exposure to air. Its nitrosochloride melts at  $142^{\circ}$ , and although repeatedly crystallised from methyl alcohol, does not change in melting point:

0.1526 gave 0.1503 AgCl. Cl = 24.37.

$\text{C}_6\text{H}_8\text{ONCl}$  requires Cl = 24.39;  $\text{C}_6\text{H}_{10}\text{ONCl}$  requires Cl = 24.07 per cent.

The nitrosochloride of tetrahydrobenzene melts at  $152-153^{\circ}$  (Baeyer, *ibid.*, p. 109). When oxidised with potassium permanganate, the liquid, boiling at  $81-82^{\circ}$ , gave small quantities of succinic and adipic acids; the latter, which melted at  $148^{\circ}$ , was analysed:

0.1249 gave 0.2248  $\text{CO}_2$  and 0.0749  $\text{H}_2\text{O}$ . C = 49.08; H = 6.66.

$\text{C}_6\text{H}_{10}\text{O}_4$  requires C = 49.31; H = 6.85 per cent.

The mixture of hydrocarbons (b. p. 81—82°) rapidly decolorises a solution of bromine in chloroform, the amount of bromine absorbed corresponding approximately to 2 atoms :

1·0400 absorbed 1·804 Br. Molecular absorption = 138·6.

1·0516 „ 1·766 Br. „ „ = 134·5.

$C_6H_8$  requires 160 for  $Br_2$  and 320 for  $2Br_2$ .

On evaporating the chloroform on the water-bath, there resulted a slightly coloured liquid, which did not evolve hydrogen bromide even after remaining for some time in a desiccator over calcium chloride. From the liquid, fern-like clusters of long, transparent needles slowly separated; these were purified by crystallisation from light petroleum, and analysed :

0·1618 gave 0·1796  $CO_2$  and 0·0492  $H_2O$ . C = 30·27 ; H = 3·38.

0·1138 „ 0·1794 AgBr. Br = 67·08.

0·1072 „ 0·1686 AgBr. Br = 66·92.

$C_6H_8Br_2$  requires C = 30·00 ; H = 3·30 ; Br = 66·66 per cent.

*Dibromodihydrobenzene* is readily soluble in the cold in chloroform, benzene, or acetone, and in alcohol or light petroleum (b. p. 40—60°) on heating. It crystallises from the latter solvent in clusters of needles, or, on slow crystallisation, in transparent, hexagonal prisms melting at 104·5°. When exposed to air, it slowly decomposes, more rapidly *in vacuo* or on heating at 170°, when hydrogen bromide and a vapour burning with a smoky flame are evolved. If the substance be maintained at a temperature of 170°, the whole gradually disappears, and if the heating is at any time interrupted, the residue solidifies on cooling, and consists of unaltered material melting at 104°. It would appear, therefore, that the substance is decomposed on heating into hydrogen bromide and benzene, but the correctness of this supposition has so far not been definitely proved.

Dibromodihydrobenzene decolorises a solution of potassium permanganate slowly in the cold, and readily on warming. A complete investigation of the products of this reaction and of the properties of dibromodihydrobenzene will be undertaken when a larger supply of material has been obtained.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has in part defrayed the expenses of this investigation.

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LVII.—*Essential Oil of Hops.*

By ALFRED C. CHAPMAN.

IN former communications to the Society (Proc., 1893, 9, 177; Trans., 1895, 67, 54, and 780), I have dealt with the results obtained by distilling the oil of hops fractionally under reduced pressure, and have described the preparation and properties of the sesquiterpene, humulene, and some of its more important derivatives.

At the time when an account of the above work was given, the hydrocarbon of lower boiling point had not been identified, and no conclusion was arrived at with regard to the nature of the small fraction or fractions boiling at temperatures intermediate between the boiling points of that hydrocarbon and humulene. Circumstances, which compelled me to relinquish the work temporarily, occasioned the delay which has occurred in presenting an account of the complete investigation to the Society. In this work I have made use of three additional samples of oil, which I shall refer to by the numbers 5, 6, and 7, in order to bring them into line with the four samples already investigated. The first was distilled by Messrs. Schimmel and Co., of Miltitz, near Leipzig, from Bavarian hops grown in 1894. The second was distilled for me by Messrs. Schimmel from Californian hops (yield = 0.53 per cent.) grown in 1899, and purchased in this country. No. 7 was distilled by Messrs. Schimmel & Co. from Bavarian hops grown in 1901, and the genuineness of the three samples is consequently entirely above suspicion. I desire to take this opportunity of expressing to this firm my best thanks for their kindness and courtesy.

The three samples had the following specific gravities and specific rotatory powers:

|             | Sp. gr.<br>15°/15°. | Sp. gr.<br>20°/20°. | $[\alpha]_D^{20^\circ}$ . |
|-------------|---------------------|---------------------|---------------------------|
| No. 5 ..... | 0.8676              | 0.8645              | + 0.30°                   |
| No. 6 ..... | 0.8639              | 0.8610              | - 0.20°                   |
| No. 7 ..... | 0.8403              | 0.8357              | - 0.08°                   |

No. 5 was almost entirely used for the study of the oxidation products of the oil, and need not be more particularly referred to at present.

The Californian oil (No. 6), after a long series of fractional distillations under 46 mm. pressure, was resolved into the following six fractions which had the sp. gr. (15°/15°) indicated.

|                           |                           |
|---------------------------|---------------------------|
| (1) 82—84° sp. gr. 0.8046 | (2) 85—92° sp. gr. 0.8108 |
| (3) 95—120° „ 0.8298      | (4) 120—130° „ 0.8638     |
| (5) 135—150° „ 0.8925     | (6) 155—160° „            |

The third sample of oil (No. 7) was similarly fractionated under 33 mm. pressure, and gave the following five fractions:—(1) 76—78°, (2) 80—85°, (3) 115—130°, (4) 130—140°, (5) 140—150°.

In both cases the first and the last fractions were by far the largest, amounting together to more than 80 per cent. of the original oil. The last fractions (No. 6 of the second oil and No. 5 of the third) consisted of nearly pure humulene, and need not be further referred to, except to say that after purification they were used in the oxidation experiments of which an account is given in the latter part of this paper.

The first fraction in the case of each oil amounted to nearly 50 per cent. of the sample taken, and as these were found to be identical in composition, one description of the experimental investigation will suffice.

#### *The Fraction of Lowest Boiling Point.*

At the time when my first paper on this subject was published, I had obtained similar fractions from the oils then examined, and had arrived at the conclusion that they consisted of a mixture of an "olefinic terpene" with a hydrocarbon having the formula  $C_{10}H_{18}$ , the statement in regard to the existence of the latter substance being based on the percentage of hydrogen found on analysis.

Having obtained a much larger quantity of this fraction from the two samples of oil above referred to, I was anxious to purify it as completely as possible with the object of ascertaining whether I could obtain more definite evidence of the existence of the hydrocarbon  $C_{10}H_{18}$ . To this end it was submitted to repeated distillation over bright sodium under reduced pressure until the metal remained quite unaltered. In this way a considerable quantity of liquid of practically constant boiling point was obtained, although it was not found possible to remove the last trace of oxygen.

The following are the results of two combustions :

0.2147 gave 0.6908  $CO_2$  and 0.2263  $H_2O$ . C = 87.75, H = 11.71.

0.2222 „ 0.7125  $CO_2$  „ 0.2357  $H_2O$ . C = 87.45; H = 11.77.

$C_{10}H_{16}$  requires C = 88.23; H = 11.77 per cent.

It will be observed that in both analyses the percentage of carbon is slightly lower than that demanded by theory, but this is unquestionably due to the rapidity with which the hydrocarbon oxidises in air, and to the impossibility of removing the last trace of oxygen by distillation over sodium. Other hydrogen estimations gave 11.80, 11.82, 11.74, and 11.83, so that there can be no doubt that the fraction consists of one compound having the formula  $C_{10}H_{16}$ .

The hydrocarbon has sp. gr. 0.8046 at 15°/15° and 0.8020 at 20°/20°; it boiled at 74—75° (33 mm.) and at 166—168° under atmospheric pressure (774 mm.), but in the latter case there was some slight decomposition towards the end of the distillation, a small quantity of very viscous liquid remaining in the flask. It was optically inactive and a determination of its index of refraction at 20° gave the value  $n_D = 1.4645$ , whence the molecular refractive energy is 46.8, the calculated number being 46.78 for  $C_{10}H_{16}$  with 3 ethylene linkings. This compound is therefore an aliphatic hydrocarbon, and its properties are almost identical with those of myrcene, which was first obtained from bay oil by Power and Kleber, and which has since been identified in the oil of sassafras leaves.

A comparison of the constants of these two substances will make this clearer:

|   | Hydrocarbon<br>from hop oil. | Myrcene from<br>bay oil. |
|---|------------------------------|--------------------------|
| Specific gravity at 15° .....           | 0.8046                       | 0.8023                   |
| Boiling point (atmospheric pressure)... | 166—168°                     | 167°                     |
| Molecular refractive energy .....       | 46.8                         | 47.1                     |
| Action on polarised light .....         | Inactive                     | Inactive                 |

It has a very characteristic odour, which Dr. Power, to whom I sent a specimen, informs me is very similar to that of the myrcene from bay oil, and oxidises with great readiness when exposed to the air, becoming ultimately converted into a colourless resin.

From basil oil, van Romburgh has recently (Schimmel and Co., *Report*, April—May, 1901, 12) isolated an "olefinic terpene" closely resembling myrcene in its general properties, but which is stated to oxidise more readily in the air, and to which the name *ocimene* has been given. Van Romburgh states that when a small quantity is placed in a tube with oxygen over mercury "the latter rises rapidly, and after a short time the oxygen has disappeared and the tube is completely filled with mercury." A similar experiment was made with the freshly distilled hydrocarbon from hop oil, 1 c.c. being introduced into a graduated tube standing over mercury and containing 20 c.c. of oxygen. Absorption took place slowly, and at the end of three days at the ordinary room temperature, 16 c.c. of oxygen had united with the hydrocarbon, and the action was still proceeding. The words "rises rapidly" could scarcely be employed in referring to the rise of the mercury due to oxygen absorption in this experiment, and on the other hand, van Romburgh's statement that he had kept myrcene prepared from bay oil for many months without being able to detect any change requires to be supplemented by a statement of the conditions under which the hydrocarbon was kept. The hydrocarbon



from hop oil, when sealed up in a tube from which the air has been exhausted, can apparently be kept for a long time without appreciable alteration, but, as I have already stated, it rapidly changes when exposed to air. Van Romburgh's statement as to the stability of myrcene in air is not only opposed to Power and Kleber's observations, and to the recent experiments of Harries (*Ber.*, 1903, 35, 3259), but is scarcely in accordance with the well-known diminution of solubility which bay oil undergoes on storage. The existing accounts of the oxidisability and tendency to polymerisation of myrcene are discrepant, and no well-defined differences between the two unsaturated hydrocarbons obtained respectively from bay oil and from basil oil, either in regard to their physical constants or to their chemical properties (other than the degree of readiness with which they are said to unite with oxygen), have yet, so far as I can ascertain, been published. The investigation of ocimene is being continued, and pending the publication of further results, it would be wiser, I think, to reserve judgment in regard to the chemical individuality of that hydrocarbon.

When hydrated by means of acetic and sulphuric acids (Bertram's method), the hop oil fraction behaved like myrcene, yielding an alcohol (? myrcenol), an oil having an odour of lavender, and a hydrocarbon, which could not, however, be identified with dipentene. When oxidised with alkaline potassium permanganate solution, it gave acetic and oxalic acids and carbon dioxide, whilst with chromic acid mixture, succinic acid was obtained, together with a small quantity of an oily acid having an odour strongly resembling that of valeric acid. Myrcene was present in the last three samples of oil to the extent of from 40 to 50 per cent., but the actual proportion in any sample is doubtless dependent on the climatic and storage conditions to which the hops had been subjected, and more particularly to the manner in which they were distilled. Old samples of oil will naturally contain less myrcene than newer ones, and the solubility and specific gravity of the oil, which are so greatly influenced by the amount of this constituent present, cannot consequently be regarded as of much importance as analytical "constants" in arriving at an opinion as to the genuineness of any sample. Oil No. 1, for example, had at 15° a sp. gr. 0.880, whilst that of No. 7 was at the same temperature only 0.840. That the resinification of myrcene is very largely due to oxidation and not to simple polymerisation is shown by the fact that it retained its mobility at the end of two years when sealed up in a tube from which all the air had been exhausted.

Attempts to prepare compounds with hydrogen chloride, bromine, nitrosyl chloride, and other reagents were in all cases unsuccessful. It may be mentioned that in no case does the amount of bromine which unites with the hydrocarbon correspond with the presence of

three double linkages, but this may well be due to the polymerisation which myrcene appears to undergo so readily.

*Fractions 2 and 3 (Oil No. 6) and Fraction 2 (Oil No. 7)* consisted of mixtures of myrcene with a small quantity of the fractions of higher boiling point, but were too small to be further separated by distillation.

*Fraction 4 (Oil No. 6) and Fraction 3 (Oil No. 7)*, which were found to be practically identical in composition, formed a colourless, mobile liquid possessing a powerful and fragrant odour, but only a few c.c. were obtained.

(1) 0.1333 gave 0.3819  $\text{CO}_2$  and 0.1380  $\text{H}_2\text{O}$ .  $\text{C} = 78.13$ ;  $\text{H} = 11.50$ .

(2) 0.1702 „ 0.4860  $\text{CO}_2$  „ 0.1790  $\text{H}_2\text{O}$ .  $\text{C} = 77.87$ ;  $\text{H} = 11.69$ .

(3) 0.1900 „ 0.5344  $\text{CO}_2$  „ 0.2023  $\text{H}_2\text{O}$ .  $\text{C} = 76.70$ ;  $\text{H} = 11.84$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.92$ ;  $\text{H} = 11.68$  per cent.

1 and 2 show the composition of fraction 4 from oil No. 6, and 3 that of fraction 3 from oil No. 7.

The product, which had a sp. gr. 0.8571 at  $20^\circ/20^\circ$ , produced a rotation  $[\alpha]_D = -0.40'$ , and united readily with bromine. The quantity of this fraction obtained, even when working with 500 c.c. of the hop oil, was so small that further experiments were impossible, but there can be very little doubt that it consisted of inactive linalool mixed with a little of some active substance.

The next higher fraction was also very small, and had a less fragrant odour than the preceding one. A preliminary experiment having shown that the oil consisted of, or contained, an ester, it was saponified by boiling with alcoholic potash and then distilled in steam. The residue, after acidification with sulphuric acid and extraction with ether, yielded a small quantity of an oily acid practically insoluble in water, and possessing a powerful odour recalling that of valeric and pelargonic acids. The ethereal solution, when dried over calcium chloride and distilled from a very small fractionating flask under a pressure of 11 mm., yielded about 2 c.c. boiling near  $130^\circ$ :

0.1545 gave 0.3813  $\text{CO}_2$  and 0.1444  $\text{H}_2\text{O}$ .  $\text{C} = 67.31$ ;  $\text{H} = 10.38$ .

$\text{C}_9\text{H}_{18}\text{O}_2$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

It gave a white, curdy silver salt, which, after drying over sulphuric acid in an exhausted desiccator, gave the following results with two different preparations:

(1) 0.2588 gave 0.1024 Ag.  $\text{Ag} = 39.57$ .

(2) 0.2240 „ 0.0920 Ag.  $\text{Ag} = 41.07$ .

$\text{C}_9\text{H}_{17}\text{O}_2\text{Ag}$  requires  $\text{Ag} = 40.52$  per cent.

Sodium hydroxide (prepared from sodium) containing 0.0025



gram Na per c.c. was run into a solution of the acid in dilute alcohol, phenolphthalein being used as indicator. 0.1659 gram acid required for neutralisation 9.4 c.c. sodium hydroxide solution (= 0.0235 gram Na). For a monobasic acid of the formula  $C_9H_{18}O_2$ , 0.0241 gram Na would be required.

The crystalline sodium salt dried at  $100^\circ$  was analysed with the following result :

0.2687 gave 0.1109  $Na_2SO_4$ . Na = 13.3.

$C_9H_{17}O_2Na$  requires Na = 12.78 per cent.

This acid does not solidify, even when cooled in a freezing mixture of salt and ice, and is evidently isononoic acid, which is said to remain liquid at  $-11^\circ$  (Kullhem, *Annalen*, 1874, 173, 319).

The distillate obtained in the preparation of the above acid was thoroughly shaken with ether, and this together with the extracted ethyl alcohol was evaporated. A small quantity of a colourless mobile liquid remained, having a strong odour of linalool. Well-formed crystals slowly separated when powdered calcium chloride was added to the cooled product. Dry ether was then added, and the crystalline substance with the excess of calcium chloride collected and treated with hot water, when a very small quantity of an oil separated ; this product, which had a strong odour of geraniol, could not be further examined. After distilling off the ether from the filtrate, some liquid remained which had a strong odour of linalool, and which yielded crystals of terpin hydrate on shaking for some days with dilute sulphuric acid. The ester would, therefore, appear to be the linalyl isononoate. These alcohols and esters occur in the essential oil of hops in very small proportions, and their separation in a state of even moderate purity is consequently an exceedingly difficult and expensive matter. From both samples of oil, nearly pure humulene was obtained by fractional distillation, to the extent of about 40 per cent. It will be observed that the proportion of humulene obtained from the earlier samples of oil with which I worked was considerably higher than the above, but this is due to the fact that those samples were not examined immediately after their distillation from the plant, as was the case with Nos. 6 and 7, and consequently much polymerisation of the myrcene had occurred. Since all were distilled in steam immediately prior to fractionation, and the altered myrcene thus eliminated, the proportion of humulene would obviously be much increased.

#### *Oxidation of the Oil.*

In my earlier paper (*Trans.*, 1895, 67, 54), a few oxidation experiments with some of the fractionated constituents of the oil were



referred to, but the action of oxidising agents on the oil itself was not discussed.

*Oxidation with Chromic Acid Mixture.*—Ten c.c. of the oil were added to a mixture of 60 grams of potassium bichromate, 45 c.c. of sulphuric acid, and 200 c.c. of water, and the whole was boiled under a reflux condenser until all the chromic acid was reduced. A further quantity of chromic acid mixture was then added, and the oxidation continued for about 24 hours. The product was subsequently filtered through muslin to remove a small quantity of unattacked resin, the slight excess of chromic acid reduced by the cautious addition of sulphurous acid, the resulting solution then distilled in steam until practically the whole of the volatile acids had distilled over, and the residue in the flask after dilution was thoroughly extracted with ether, which on evaporation left a small quantity of an oily substance from which crystals separated on standing. The acid distillate was neutralised with potassium carbonate and evaporated to dryness in order to obtain the mixed potassium salts.

Numerous oxidation experiments were made, the composition of the oxidising mixture being occasionally slightly varied. In this way the potassium salts (representing the volatile acids) and the residues from the ethereal extracts of the fixed oxidation products were thus accumulated in sufficient quantity for examination. The potassium salts were dissolved in water, the acids liberated by the addition of sulphuric acid, and extracted from the solution by means of ether; after removing the solvent, the acids were distilled from a small flask under reduced pressure. The first and larger fraction consisted of nearly pure acetic acid, yielding a silver salt containing 64.1 per cent. of silver (silver acetate requires  $\text{Ag} = 64.46$ ); the second was evidently a mixture, whilst the third, which was very small, had a strong odour of valeric acid, and gave a silver salt containing 49.4 per cent. of the metal (silver valerate requires  $\text{Ag} = 51.44$ ). Several other salts were prepared from this fraction, the properties of which closely resembled those of the corresponding valerates.

Another quantity of the purified potassium salts was fractionally precipitated with silver nitrate, and 5 silver salts were obtained, containing from 64.42 (acetate) to 44.9 per cent. of silver. From this it is evident that an acid (probably isononoic) was present, having a salt containing a smaller percentage of silver than the corresponding valerate.

Although the united residues obtained after evaporating off the ether used for the extraction of the non-volatile oxidation products from the chromic acid mixture, partially crystallised on long standing, yet, as it was found impossible to recrystallise without serious loss owing to the considerable quantity of uncrystallisable oil present, it was thought better to attempt to distil the whole under reduced

pressure. From  $130^{\circ}$  to  $160^{\circ}$  (under 30 mm. pressure) an oily liquid distilled over, but the distillate obtained at  $165^{\circ}$  commenced to solidify in the condenser tube, and the receiver was consequently changed. At  $200^{\circ}$ , all the crystalline substance appeared to have distilled, and only a small quantity of a red decomposition product having a strong empyreumatic odour came over. The first oily fraction slowly solidified completely to a crystalline mass, and both acids were purified by repeated crystallisation from water. These are referred to as No. 1 and No. 2.

No. 1 consisted of well-formed, needle-shaped crystals, easily soluble in water, acetone, alcohol, and ether, and somewhat less soluble in hot benzene, from which it crystallised readily in small, colourless needles.

After two crystallisations from benzene, it melted sharply at  $140^{\circ}$ .

0.1749 gave 0.3140  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ .  $\text{C} = 48.96$ ;  $\text{H} = 6.93$ .

0.1611 ,, 0.2893  $\text{CO}_2$  ,, 0.0960  $\text{H}_2\text{O}$ .  $\text{C} = 48.97$ ;  $\text{H} = 6.63$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C} = 49.31$ ;  $\text{H} = 6.85$  per cent.

*Titration of the Acid.*—Sodium hydroxide (prepared from sodium) containing 0.004669 gram Na per c.c. was run into an aqueous solution of the acid, phenolphthalein being used as indicator. 0.2015 gram acid required for neutralisation 13.7 c.c. sodium hydroxide solution ( $= 0.0639$  gram Na). For a dibasic acid of the formula  $\text{C}_6\text{H}_{10}\text{O}_4$ , 0.0634 gram Na would be required.

When solutions of the metallic salts indicated below were added to an aqueous solution of the sodium salt, the following results were obtained:

|                         |                                   |                       |                                 |
|-------------------------|-----------------------------------|-----------------------|---------------------------------|
| Magnesium sulphate.     | No reaction                       | Lead acetate .....    | On warm-                        |
| Calcium chloride.....   | No reaction                       |                       | ing, a dense white precipitate. |
| Barium chloride .....   | No reaction                       | Copper sulphate ..... | On warm-                        |
| Silver nitrate .. ..... | White gran-                       |                       | ing, a green precipitate.       |
|                         | ular precipitate slightly soluble |                       |                                 |
|                         | in water.                         |                       |                                 |

Two preparations of the silver salt, dried at  $100^{\circ}$ , gave 59.5 and 60.0 per cent. Ag respectively.  $\text{C}_6\text{H}_8\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 59.78$ . The iron salt dried at  $100^{\circ}$  was found to contain 21.0 per cent. Fe.  $(\text{C}_6\text{H}_8\text{O}_4)_3\text{Fe}_2$  requires  $\text{Fe} = 20.58$ . All the above results show that this acid is unsymmetrical dimethylsuccinic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{Me})_2 \cdot \text{CO}_2\text{H}$ .

*No. 2 Acid.*—This acid crystallised well from water or alcohol, and gave all the reactions of succinic acid; the crystals from the latter solvent melted at  $184^{\circ}$ .

0.161 gave 0.2425  $\text{CO}_2$  and 0.0756  $\text{H}_2\text{O}$ .  $\text{C} = 41.06$ ;  $\text{H} = 5.22$ .

$\text{C}_4\text{H}_6\text{O}_4$  requires  $\text{C} = 40.68$ ;  $\text{H} = 5.08$  per cent.

The oxidation products of the oil obtained by the action of chromic acid mixture are, therefore, acetic, valeric, dimethylsuccinic, and succinic acids, with probably isononoic acid from the linalyl ester.

When an alkaline solution of potassium permanganate was used instead of chromic acid mixture for the oxidation, all the above oxidation products were identified with the exception of the dimethylsuccinic acid, and oxalic acid was found in considerable quantity when dilute nitric acid was employed.

It may be well to correct a very common belief that valeric acid is a product of the aerial oxidation of hop oil. I have made many experiments in connection with this point, and in no instance was even a trace of valeric acid formed.

The dimethylsuccinic acid is an oxidation product of humulene, as was proved by submitting the purified sesquiterpene to the action of the chromic acid mixture, and isolating the products in the same manner as in the hop oil experiments. Along with that acid (m. p. =  $140^{\circ}$ ), acetic acid was found in considerable quantity, together with a little valeric acid, mixed apparently with some higher homologue.

Myrcene, on oxidation, yielded chiefly acetic acid with some succinic acid; levulinic acid could not be identified.

It is interesting to note that dimethylsuccinic acid, to the extent of about 1.5 per cent., was obtained by Levy and Engländer (*Ber.*, 1885, 18, 3209) by the oxidation of caryophyllene from copaiba balsam by means of chromic acid solution. Owing to the small yield, the above-named authors doubted whether this acid was to be regarded as an oxidation product of the caryophyllene itself, or whether it might not have been due to the presence of some unrecognised impurity. The fact that this acid has also been obtained from carefully purified humulene supports the former view, and it will be interesting to note whether it is an oxidation product of sesquiterpenes in general. On this point, I propose to make further experiments.

The essential oil of hops, therefore, contains the following compounds: myrcene, humulene, linalool, linalyl isononoate, probable traces of some ester of geraniol, and a small amount of a diterpene.

In all the freshly distilled samples of oil examined by me, the hydrocarbons, myrcene and humulene, were present to the extent of from 80 to 90 per cent.

In conclusion, I desire to offer my sincere thanks to my assistants, Messrs. P. H. Carpenter and Theo. C. Thomas, for much valuable help in connection with this work.

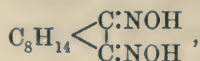
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LVIII.—*Studies in the Camphane Series. Part XI. The Dioximes of Camphorquinone and other Derivatives of isoNitrosocamphor.*

By MARTIN ONSLOW FORSTER.

TEN years have elapsed since Manasse (*Ber.*, 1893, 26, 243) described three isomeric dioximes having the constitution



produced by the action of hydroxylamine on *isonitrosocamphor*. A variety of interesting facts concerning the monoxime of camphor have come to light since that time, suggesting directions in which the investigation of the dioximes might be profitably extended. On preparing specimens of these substances, however, it was found that the existing description must be modified in several important particulars.

The three isomerides obtained by Manasse were distinguished from one another as the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -dioximes, melting at 181–182°, 220–221°, and 131–132° respectively; in the meantime, a  $\delta$ -dioxime, melting at about 245°, has been described by Angelico (*Atti R. Accad. Lincei*, 1900, [v], 9, ii, 47). Neither of the investigators mentioned appears to have determined the rotatory power of the dioximes, and on submitting to fractional crystallisation the mixture obtained from *isonitrosocamphor* and hydroxylamine acetate, examining each fraction in the polarimeter, I found that the melting points recorded by Manasse are considerably lower than those of the purified substances. The  $\beta$ -dioxime, for example, melts and decomposes at a temperature fully 25° above that mentioned by Manasse, and it became evident that Angelico's supposed  $\delta$ -dioxime is a comparatively pure specimen of Manasse's  $\beta$ -dioxime. Although this observation reduces to three the number of existing dioximes, I have discovered a fourth isomeride which has properties quite distinct from those of the foregoing substances, and in future this derivative will be called the  $\delta$ -dioxime. The table on p. 515 summarises the chief characteristics of the four compounds.

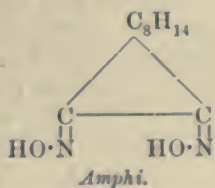
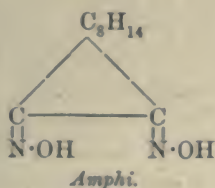
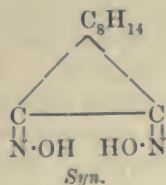
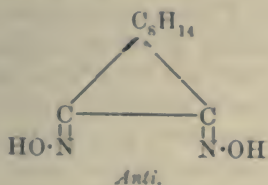
I am indebted to Dr. Lowry for a report on the crystallography of the  $\alpha$ -,  $\beta$ -, and  $\delta$ -dioximes, from which it appears that the last-named is quite distinct from the  $\alpha$ -modification, the only one for which it might possibly be mistaken.

At an early stage in the examination of these substances, it was found that no reliance could be placed on the melting point as a means of identification, because in each case fusion is attended by profound

|                   | M. p. | $[\alpha]_D$ in alcohol. | $[\alpha]_D$ in 2 per cent. sodium hydroxide. | Precipitate with sodium hydroxide and ferrous sulphate. | Absolute alcohol required to dissolve 1 gram at 20°. |
|-------------------|-------|--------------------------|---|---|--|
| $\alpha$ -Dioxime | 201°  | -63.6°                   | -98.3°  | chocolate   | 40.0 c.c.  |
| $\beta$ -Dioxime  | 248   | →                        | -24.1   | chocolate   | 590.0  |
| $\gamma$ -Dioxime | 135   | +22.4                    | +12.6   | none  | 1.0  |
| $\delta$ -Dioxime | 199   | +75.5                    | +83.6   | chocolate   | 12.4   |

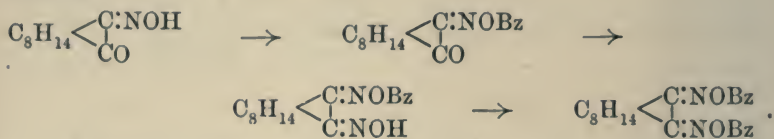
change, the point at which this occurs being considerably modified by admixture, and to some extent also by the rate at which the temperature rises. The  $\alpha$ -,  $\beta$ -, and  $\delta$ -dioximes evolve gas vigorously at the melting point, whilst the  $\gamma$ -dioxime is converted into the newly discovered  $\delta$ -modification, and not, as stated by Manasse, into the  $\alpha$ -dioxime. The specific rotatory power is the most satisfactory constant to employ in the identification of the four isomerides.

The Hantzsch-Werner hypothesis, when applied to the case of the camphorquinonedioximes, predicts four possible isomerides, related to one another as follows :



In this respect camphorquinone differs from benzil, from which three dioximes only have been obtained, the  $C_8H_{14}$ -residue being unsymmetrical, and therefore yielding two *amphi*-modifications. This is the first recorded instance of the four dioximes of an unsymmetrical diketone having been isolated, but in the present paper no attempt will be made to assign to each modification its respective configuration, as the experiments having this object are still incomplete. In considering the question, it was thought that some information might be gained by comparing the products of direct benzylation with the derivative

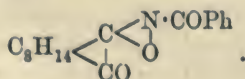
obtained from *isonitrosocamphor* in the manner represented by the formulæ :



On subjecting *isonitrosocamphor* to benzylation by the Schotten-Baumann process, however, there were obtained, in approximately equal amounts, two compounds having the empirical formula of a benzoyl*isonitrosocamphor*. One of these substances is bright yellow, and when hydrolysed yields *isonitrosocamphor* mixed with benzoic acid ; the isomeride, on the other hand, is colourless, and is converted on hydrolysis into benzoic and  $\alpha$ -camphornitrilic (cyanolauronic) acids. Hence it is evident that the yellow compound alone is a genuine benzoyl derivative of *isonitrosocamphor*.

The constitution of the colourless *pseudobenzoyl* derivative is not so easily determined. The first explanation which suggests itself is one depending on the possibility of *isonitrosocamphor* exhibiting stereoisomerism, but it is unlikely that of two *isonitrosocamphors* related in this manner, the benzoyl derivative of one should be bright yellow, whilst that of the other is snow white ; moreover, if the colourless substance is the benzoyl derivative of a stereoisomeric *isonitrosocamphor*, it would be reasonable to expect that, even should the latter be incapable of free existence, some proportion of the known modification would be formed on hydrolysis, whereas the conversion into  $\alpha$ -camphornitrilic acid is complete. The possibility of *isonitrosocamphor* exhibiting stereoisomerism has been already considered by Oddo (*Ber.*, 1895, 28, 1915), who encountered differences in the properties of *isonitrosocamphor* obtained by the method of Claisen and Manasse when compared with those of specimens produced from camphorcarboxylic acid and sodium nitrite. Oddo (*loc cit.*) mentions that *isonitrosocamphor* from both sources yields a benzoyl derivative which melts at 127—128°, and this is probably identical with the colourless substance, melting at 136°, described in the present paper, although there is no evidence that Oddo's compound is not also a genuine benzoyl derivative of *isonitrosocamphor*.

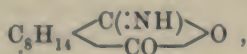
In the second place, it is conceivable that the colourless benzoyl compound is derived from an *isooxime* of camphorquinone, when it would be represented by the formula



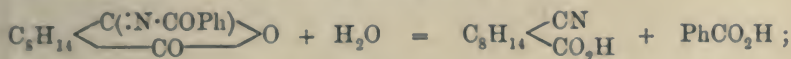


This view accords with the fact that the substance is susceptible to the action of light and of alkalis, for Dunstan and Goulding have recently shown (*Trans.*, 1901, 79, 628) that alkyl derivatives of the *isooximes* are extremely sensitive towards hydrolytic agents.

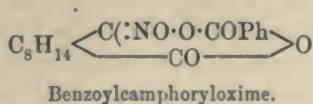
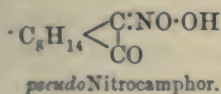
An explanation more probable than either of these, however, would represent the *pseudobenzoyl* derivative of *isonitrosocamphor* as being related to camphorisoimide,



a substance isolated in the form of its hydrochloride when  $\alpha$ -camphornitrilic acid, dissolved in ether, is treated with hydrogen chloride (Oddo and Leonardi, *Gazzetta*, 1896, 26, i, 405), or by the action of acetyl chloride on  $\alpha$ -camphoramic acid (Hoogewerff and van Dorp, *Rec. Trav. Chim.*, 1895, 14, 252). Such a structure accounts for the production of benzoic and  $\alpha$ -camphornitrilic acids on hydrolysis:



but, unfortunately, owing to the readiness with which camphorisoimide hydrochloride becomes hydrolysed by alkalis, it has not been possible to prove this point experimentally. A further argument in favour of this representation, however, may be drawn from the behaviour of nitrocamphor, which yields benzoylcamphoryloxime (Lowry, *Trans.*, 1898, 73, 986):



In view of the change which *isonitrosocamphor* undergoes when benzoyl chloride acts on solutions in caustic alkalis, the behaviour of the dried alkali derivatives towards acyl chlorides has been studied, and this has brought to light a compound which appears to be the anhydride of *isonitrosocamphor*. It is a pale yellow substance, which melts at about 190°, undergoing conversion into the colourless anhydride of  $\alpha$ -camphornitrilic acid,

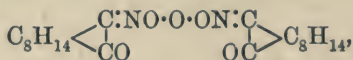


which is obtained also by the action of acetyl chloride on *isonitrosocamphor* (Oddo, *Ber.*, 1895, 28, 1915; Oddo and Leonardi, *loc. cit.*).

It is somewhat remarkable that the new anhydride has escaped the attention of previous workers in this field, because it may be obtained in a variety of ways. Small quantities are produced when the dry alkali derivatives of *isonitrosocamphor* are treated with acetyl chlor-

ide, benzoyl chloride, phosphorus oxychloride, and acetic anhydride, whilst the last-named agent, when added to a solution in sodium hydroxide, converts 10 per cent. of the *isonitrosocamphor* employed into the anhydride. The most satisfactory method of preparing this compound, however, is to heat together the potassium and benzoyl derivatives of *isonitrosocamphor* in a non-hydroxylic solvent, a process which affords useful evidence as to the constitution of the substance.

Anhydrides of this type are scarcely known, the only comparable substance to which I can find any reference being benzaldoxime anhydride,  $(C_6H_5 \cdot CH:N)_2O$ , obtained by Bamberger and Szolayski on passing air through a suspension of  $\beta$ -benzylhydroxylamine in water (*Ber.*, 1900, 33, 3193). It is noteworthy that the anhydride of *isonitrosocamphor* closely resembles in appearance the anhydride of *pseudonitrocaphor*, and melts at the same temperature (*Lowry, Trans.*, 1898, 73, 996),



but the two substances are quite distinct in general behaviour, for whilst alcoholic potash resolves the last-named into camphorquinone, the anhydride of *isonitrosocamphor* is converted into  $\alpha$ -camphornitrilic acid.

Somewhat unexpectedly, the present investigation has led to the discovery of the missing form of *isonitrosocamphor*. It has been mentioned that by the ordinary process of benzylation, the camphor derivative yields two substances, of which the genuine benzoyl*iso*-nitrosocamphor is yellow, whilst the *pseudo*-compound is colourless. When *m*-nitrobenzoyl chloride is allowed to act on *isonitrosocamphor* under the same conditions, a yellow compound is formed, also in association with a colourless isomeride. If the former product is hydrolysed with the theoretical amount of caustic potash dissolved in alcohol, ordinary *isonitrosocamphor* is regenerated, but on using excess of alkali, a new modification arises, melting at  $114^\circ$  instead of  $152^\circ$ . It is distinguishable from the common modification in other ways, but resembles the latter in developing a yellow colour with alkalis, and in yielding camphorquinone when treated with nitrous acid. The substance must be regarded as an unstable form of *isonitrosocamphor*, because when it is heated above  $114^\circ$  the product solidifies before the melting point of the better known modification is reached, and melts again at  $152$ — $153^\circ$ .

The investigation of this interesting substance is being continued with the object of explaining its relationship to the stable isomeride, and it is hoped that the behaviour of the compound towards hydroxylamine may assist in determining the configuration of the four dioximes.

The action of other acyl chlorides on isonitrosocamphor is being studied also, and the results will be communicated in a subsequent paper.

## EXPERIMENTAL.

### *The Dioximes of Camphorquinone.*

When isonitrosocamphor, dissolved in alcohol, is heated with hydroxylamine hydrochloride and sodium acetate, the  $\alpha$ - and  $\beta$ -dioximes are the chief products, along with about 10 per cent. of the newly discovered  $\delta$ -modification. The  $\gamma$ -dioxime is produced alone when isonitrosocamphor, dissolved in aqueous sodium hydroxide, remains with free hydroxylamine during several days at 40–50°, whilst the  $\delta$ -dioxime is formed when the  $\gamma$ -modification is fused (135°), or heated at 100° with absolute alcohol in a sealed tube.

*Preparation of the  $\alpha$ - and  $\beta$ -Dioximes.*—One hundred grams of isonitrosocamphor were dissolved in alcohol, to which 80 grams of hydroxylamine hydrochloride, and 160 grams of crystallised sodium acetate dissolved in the minimum quantity of hot water were added. A clear solution having been produced by means of alcohol, the liquid was heated during 5 hours, and filtered after a further interval of 12 hours. The crystalline product, after washing with cold alcohol, and extracting first with 200 c.c. of boiling alcohol, and then twice with 100 c.c. of the hot solvent, weighed 25 grams (A); it consisted chiefly of the  $\beta$ -dioxime.

The united filtrates were then distilled, and the residual liquid, when free from alcohol, diluted largely with water; the red solid thus obtained, which weighed 75 grams, was powdered and extracted four times with 250 c.c. of cold ethyl acetate (B). This solvent removed all the  $\delta$ -dioxime, leaving a residue of 25 grams, consisting of a mixture of the  $\alpha$ - and  $\beta$ -dioximes, from which the former was isolated by boiling with 1000 c.c. of ethyl acetate, filtering the liquid 24 hours after cooling, and distilling the filtrate until 500 c.c. had passed over; the residue deposited 10 grams of colourless, prismatic needles giving  $[\alpha]_D - 61.7^\circ$  in alcohol, and this product, when recrystallised from boiling alcohol, provided characteristic crystals of the  $\alpha$ -dioxime, having  $[\alpha]_D - 63.6^\circ$ .

The  $\beta$ -dioxime was obtained from the residue (A) by extracting twice with 1000 c.c. of boiling spirit, the second filtrate depositing minute, colourless prisms having  $[\alpha]_D - 26.8^\circ$  in 2 per cent. aqueous sodium hydroxide.

*Preparation of the  $\gamma$ -Dioxime.*—One hundred grams of isonitrosocamphor were dissolved in water containing 90 grams of sodium hydroxide; 100 grams of hydroxylamine hydrochloride were then dissolved in sufficient water to bring the total volume to 1000 c.c.,



and added, with continual stirring, to the alkaline liquid. After remaining in a warm place during several days, the liquid was filtered, and acidified with dilute sulphuric acid, which at first precipitated a yellow, viscous oil, followed by a colourless, crystalline solid; with a little care, it is possible to interrupt the process when the oily substance is completely separated, and in that way the  $\gamma$ -dioxime may be obtained fairly pure. Recrystallisation from boiling water, if conducted rapidly, yields minute, colourless needles, melting at  $135^{\circ}$ , and giving  $[\alpha]_D + 22.4^{\circ}$  in alcohol.

*Preparation of the  $\delta$ -Dioxime.*—The  $\delta$ -dioxime, described for the first time in this paper, occurs as a by-product in the preparation of the  $\alpha$ - and  $\beta$ -dioximes, and can be isolated from the cold ethyl acetate extracts (B) by evaporating these, recrystallising the residues from a small quantity of hot alcohol, and then extracting the product with 1700 c.c. of boiling water: this deposits crystals having  $[\alpha]_D + 40^{\circ}$ , from which cold ethyl acetate removes a small quantity of the  $\delta$ -dioxime, giving  $[\alpha]_D + 75.9^{\circ}$ .

A much more convenient method of preparing the  $\delta$ -dioxime consists in dissolving the  $\gamma$ -modification in twice its weight of alcohol, and heating the solution in a sealed tube at  $100^{\circ}$  during one hour; the colourless crystals which separate from the solution on cooling consist of the  $\delta$ -isomeride in a highly purified form. So readily does this transformation occur, that by simply evaporating to dryness a concentrated alcoholic solution of the  $\gamma$ -dioxime, a residue is obtained which consists almost entirely of the  $\delta$ -modification.

The  $\gamma$ -dioxime is also transformed by fusion. Small quantities of the substance, not exceeding 1 decigram, may be heated at  $145^{\circ}$  until completely fused; the hard, white solid obtained on cooling consists of the  $\delta$ -dioxime, giving  $[\alpha]_D + 73.5^{\circ}$  after a single crystallisation from ethyl acetate. It is somewhat difficult, however, to prepare moderate quantities of the  $\delta$ -modification by this process, as the fused  $\gamma$ -dioxime frequently changes into a yellow, uncrystallisable product if not withdrawn from the heating bath immediately on fusion.

The  $\alpha$ -dioxime is most conveniently crystallised from ethyl acetate, which deposits it in beautiful, transparent, orthorhombic prisms, which melt and decompose at  $201^{\circ}$ . Although colourless when pure, it is difficult to free the substance from a yellow stain, which is very pronounced in large crystals.

A solution containing 0.3929 gram in 25 c.c. of absolute alcohol at  $20^{\circ}$  gave  $\alpha_D - 2.0'$ , whence  $[\alpha]_D - 63.6^{\circ}$ ; 0.6465 gram dissolved in 25 c.c. of 2 per cent. aqueous sodium hydroxide gave  $\alpha_D - 5.5'$ , in a 2-dem. tube, whence  $[\alpha]_D - 98.3^{\circ}$ .

It forms a colourless solution in aqueous caustic alkali, and on

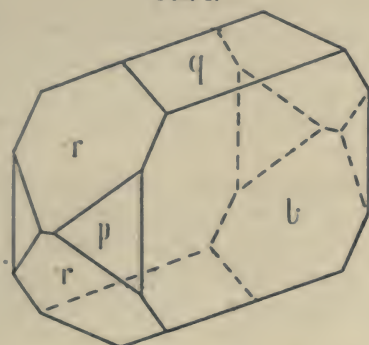
adding ferrous sulphate to this liquid a chocolate-brown precipitate is formed. When dissolved in absolute alcohol, the  $\alpha$ -dioxime develops a deep red coloration with ethereal ferric chloride. Ammoniacal silver nitrate is slowly reduced on heating, forming a mirror. Sodium carbonate solution dissolves it slowly on boiling. One gram of the substance requires for its solution 40 c.c. of absolute alcohol at  $20^\circ$ , 150 c.c. of ethyl acetate at  $18^\circ$ , 265 c.c. of chloroform at  $18^\circ$ , or 1700 c.c. of boiling water.

Dr. T. M. Lowry's crystallographic report is in the following terms

"The  $\alpha$ -dioxime was obtained in splendidly developed, sharply pointed prisms, which gave very bright images on the goniometer.

"*System*.—Orthorhombic.  $a:b:c=1.6775:1:0.5150$ .

FIG. 1.



"*Forms present*.—The crystals, which had been obtained by slow evaporation of a solution in ethyl acetate, had the general shape shown in Fig. 1, the forms present being  $b\{010\}$ ,  $p\{110\}$ ,  $q\{011\}$ ,  $r\{201\}$ . The dominant forms were  $b$  and  $r$ .

"The following angular measurements were obtained:

| Angle.                     | Number of measurements. | Limits.                         | Mean.           | Calculated      |
|----------------------------|-------------------------|---------------------------------|-----------------|-----------------|
| $bq = 010:011$             | 16                      | $62^\circ 41' - 62^\circ 49'$   | $62^\circ 45'$  | —               |
| $qq = 011:0\bar{1}1$       | 8                       | $54^\circ 16' - 54^\circ 49'$   | $54^\circ 28'$  | $54^\circ 30'$  |
| $bp = 010:110$             | 18                      | $30^\circ 40' - 30^\circ 54'$   | $30^\circ 48'$  | —               |
| $pp = 110:1\bar{1}0$       | 10                      | $118^\circ 14' - 118^\circ 34'$ | $118^\circ 23'$ | $118^\circ 24'$ |
| $br = 010:201$             | 8                       | $89^\circ 53' - 90^\circ 4'$    | $90^\circ 0'$   | $90^\circ 0'$   |
| $pr = 110:201$             | 4                       | $74^\circ 27' - 74^\circ 28'$   | $74^\circ 27'$  | $74^\circ 28'$  |
| $pr = 110:20\bar{1}$       | 4                       | $105^\circ 26' - 105^\circ 39'$ | $105^\circ 32'$ | $105^\circ 32'$ |
| $rq = 201:011$             | 7                       | $40^\circ 34' - 40^\circ 48'$   | $40^\circ 42'$  | $40^\circ 45'$  |
| $rq = 201:0\bar{1}\bar{1}$ | 7                       | $139^\circ 11' - 139^\circ 24'$ | $139^\circ 19'$ | $139^\circ 15'$ |
| $rr = 201:20\bar{1}$       | 4                       | $116^\circ 56' - 117^\circ 0'$  | $116^\circ 58'$ | $116^\circ 54'$ |
| $rr = 201:201$             | 4                       | $62^\circ 57' - 63^\circ 9'$    | $63^\circ 1'$   | $63^\circ 6'$   |

"*Cleavage*.—The crystals are very hard, and have no definite plane of cleavage, but splinter in an irregular manner.

"*Optical properties*.—The extinctions observed on examining the crystals in a parallel beam of plane-polarised light were in accordance with their orthorhombic symmetry. A brilliant biaxial figure was seen on examining, in a convergent beam of polarised light, sections cut perpendicularly to the long axis of the prism. The optic axial angle is exceptionally small, the angle for red being greater than the angle for blue light. The optic axial plane is parallel to the faces of the form {010}, and the acute bisectrix is parallel to the axis of  $a$ . The double refraction is positive in sign."

The  $\beta$ -dioxime is the most sparingly soluble of the four isomerides. It crystallises from alcohol in minute, colourless prisms, melting and decomposing vigorously at  $248^\circ$ .

Owing to the sparing solubility of the  $\beta$ -dioxime, its specific rotatory power when dissolved in organic solvents could not be determined, but a solution containing 0.4666 gram in 25 c.c. of 2 per cent. aqueous sodium hydroxide gave  $\alpha_D -54'$  in a 2-dcm. tube, whence  $[\alpha]_D -24.1^\circ$ .

It is practically insoluble in boiling sodium carbonate, and forms a colourless solution in caustic alkalis which yields a chocolate precipitate with ferrous sulphate. When boiled for some time with ammoniacal silver nitrate, slight reduction of this agent takes place. One gram of the substance is dissolved by 590 c.c. of absolute alcohol at  $20^\circ$ , 3500 c.c. of ethyl acetate at  $18^\circ$ , and 13,300 c.c. of chloroform at  $18^\circ$ .

The  $\beta$ -dioxime has been obtained also by heating an alcoholic solution of camphorquinone with hydroxylamine hydrochloride and sodium acetate dissolved in water, until the yellow colour of the liquid disappeared.

Dr. Lowry states that "the  $\beta$ -dioxime had separated from alcohol in minute prisms which were too small for crystallographic measurement. The prism faces showed extinctions parallel to the edges, and a biaxial figure was seen through a section across the prism. It is therefore probable that in this case also the crystals belong to the orthorhombic system, and that the axis of the prism is the acute bisectrix."

The  $\gamma$ -dioxime is the most soluble modification, dissolving with extraordinary readiness in alcohol, ethyl acetate, chloroform, and benzene; it separates from boiling light petroleum or water in minute, colourless needles which melt at  $135^\circ$  to a clear liquid; this becomes almost immediately turbid, and then solidifies. Crystallisation from water, however, is liable to transform a portion of the substance into



the  $\delta$ -dioxime, which separates in opaque nodules ; it was owing to this property that the  $\delta$ -isomeride was first isolated.

A solution containing 0.2513 gram in 25 c.c. of absolute alcohol at  $21^\circ$  gave  $\alpha_D 27'$  in a 2-dcm. tube, whence  $[\alpha]_D + 22.4^\circ$ ; 0.4619 gram in 25 c.c. of 2 per cent. aqueous sodium hydroxide gave  $\alpha_D 28'$  whence  $[\alpha]_D + 12.6^\circ$ .

The  $\gamma$ -dioxime dissolves readily in cold sodium carbonate, forming a colourless liquid, and the solution in caustic alkalis gives no distinctive precipitate with ferrous sulphate. When dissolved in absolute alcohol, it develops a pale brown coloration with ethereal ferric chloride ; on heating the liquid, this colour changes to deep red, and returns to pale brown on cooling. The substance does not reduce ammoniacal silver nitrate, even on boiling.

One gram of the  $\gamma$ -dioxime dissolves in 1 c.c. of absolute alcohol ; 21.219 grams of a solution concentrated at  $19^\circ$  consisted of 11.862 grams of the substance and 9.357 grams of alcohol. On evaporating this solution to dryness on the water-bath, the product gave  $[\alpha]_D + 68.4^\circ$ , showing that conversion into the  $\delta$ -dioxime was almost complete.

The  $\delta$ -dioxime, which in respect of solubility lies between the  $\alpha$ - and the  $\gamma$ -modifications, separates from ethyl acetate in transparent, cube-like crystals, and melts, evolving gas, at  $199^\circ$  :

0.2226 gave 27.8 c.c. nitrogen at  $20^\circ$  and 775 mm.  $N = 14.57$ .

$C_{10}H_{16}O_2N_2$  requires  $N = 14.28$  per cent.

A solution containing 0.2539 gram dissolved in 25 c.c. of absolute alcohol at  $21^\circ$  gave  $\alpha_D 1^\circ 32'$  in a 2-dcm. tube, whence  $[\alpha]_D + 75.5^\circ$ ; 0.4632 gram dissolved in 25 c.c. of 2 per cent. aqueous sodium hydroxide gave  $\alpha_D 3^\circ 6'$ , whence  $[\alpha]_D + 83.6^\circ$ .

It dissolves slowly in cold sodium carbonate, and forms a colourless solution in caustic alkalis, yielding a chocolate precipitate with ferrous sulphate. The solution in absolute alcohol develops a deep red coloration with ethereal ferric chloride, exactly like that produced by the  $\alpha$ -modification ; there is only very slight reduction of boiling ammoniacal silver nitrate. One gram of the substance requires 12.4 c.c. of absolute alcohol at  $20^\circ$  to dissolve it.

Dr. Lowry's description is as follows :

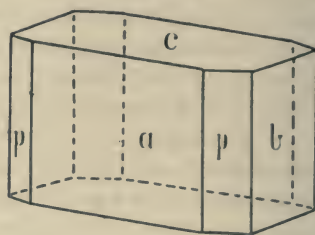
"The  $\delta$ -dioxime had separated from a solution in ethyl acetate in fairly well-formed crystals, but these gave very poor images on the goniometer, and the geometrical constants were determined only with difficulty ; the optical properties were, however, readily observed :

"*System.*—Orthorhombic.  $a : b : c = 1.116 : 1 : 0.573$ ."

FIG. 2.



FIG. 3.



" *Forms present.*— $a\{100\}$ ,  $b\{010\}$ ,  $c\{001\}$ ,  $p\{110\}$ ,  $q\{011\}$ .

" *Habit.*—Two distinct types of crystal were present, namely, (1) Crystals in which the domes  $p$  and  $q$  are the dominant forms, and the pinacoids small or absent; these are often elongated along the axis of  $c$  as shown in Fig. 2, but occasionally the development in this direction is slight, and the  $p$  faces are reduced to small triangles. (2) Cube-like crystals in which the pinacoids predominate and the dome faces appear only as small truncations on the edges of the 'cubes,' as in Fig. 3.

| Angle.                 | Number of measurements. | Limits.                         | Mean.           | Calculated.     |
|------------------------|-------------------------|---------------------------------|-----------------|-----------------|
| $qq = 011 : 0\bar{1}1$ | 4                       | $59^{\circ}31' - 59^{\circ}51'$ | $59^{\circ}38'$ | $59^{\circ}36'$ |
| $qq = 011 : 01\bar{1}$ | 4                       | $120\ 11 - 120\ 33$             | $120\ 24$       | —               |
| $pp = 110 : 1\bar{1}0$ | 7                       | $96\ 2 - 96\ 20$                | $96\ 14$        | $96\ 16$        |
| $pp = 110 : 1\bar{1}0$ | 8                       | $83\ 36 - 83\ 54$               | $83\ 44$        | —               |

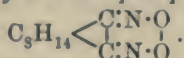
" *Cleavage.*—The crystals of this dioxime possess a very extraordinary cleavage. The main cleavage planes appear to be parallel to the faces of the form  $p\{110\}$ , and thin sheets often break away from these faces when the crystals are mounted on, or dismounted from, the wax. But there is an almost equally pronounced tendency to cleave along every other plane parallel to the vertical axis of  $c$ . So marked is the tendency to cleave in this way, that by merely rubbing a crystal between the thumb and forefinger it can be broken down into a mass of needles. Striations parallel to the axis of cleavage often appear on the faces, and the structure of the crystals may be fairly compared with that of natural asbestos or the "satin-spar" form of gypsum.

" *Optical Properties.*—In accordance with the orthorhombic symmetry of the crystals, extinctions on the pinacoid faces occur whenever the plane of polarisation is parallel to one of the square edges of the face. A biaxial figure can be seen on examining in convergent polarised light a section parallel to the form  $b\{010\}$ ; the optic axial angle is

large, and greater for blue than for red light: the optic axial plane is parallel to the form  $\alpha\{100\}$ , and the acute bisectrix is parallel to the axis of  $b$ . The double refraction is negative in sign.

"On comparing the properties of the  $\alpha$ - and  $\delta$ -dioximes, it will be seen that, in spite of their very similar structure, the crystals are altogether different. Both exhibit orthorhombic symmetry, but the axial ratios differ, the habit is entirely different, and its extraordinary cleavage distinguishes the  $\delta$ -dioxime, not only from the isomeric substances, but also from almost every other derivative of camphor that has yet been examined. The optical properties are equally distinctive, for the optic axial angle is twice as large in one case as in the other, the optic axial dispersion is in opposite directions, and the double refraction opposite in sign, in the two cases."

*The Peroxide of the Camphorquinonedioximes,*



Twenty grams of the  $\beta$ -dioxime, when dissolved in 200 c.c. of 10 per cent. potassium hydroxide, and treated with a freshly prepared ice-cold solution of 20 grams of bromine in 100 c.c. of 40 per cent. potassium hydroxide, yielded at once a white, granular precipitate, which, after an interval of 1 hour was filtered, washed, and dried (weight 19 grams). The substance, after two crystallisations from hot alcohol, was deposited in crystals resembling ammonium chloride; it melts at  $144.5^\circ$ , and immediately afterwards evolves gas:

0.1671 gave 0.3800  $\text{CO}_2$  and 0.1158  $\text{H}_2\text{O}$ .  $\text{C} = 62.02$ ;  $\text{H} = 7.70$ .

0.1620 „ 21.1 c.c. nitrogen at  $22^\circ$  and 769 mm.  $\text{N} = 14.93$ .

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{C} = 61.86$ ;  $\text{H} = 7.22$ ;  $\text{N} = 14.43$  per cent.

The same peroxide is obtained when the  $\alpha$ -dioxime is treated with hypobromite. It is slightly volatile in steam, is quite insoluble in aqueous alkalis, and does not give Liebermann's reaction for nitroso-compounds. The substance is very readily soluble in chloroform, ethyl acetate, and hot alcohol, but being only sparingly soluble in light petroleum, is most conveniently crystallised from that medium.

A solution containing 0.5008 gram in 25 c.c. of absolute alcohol at  $20^\circ$ , gave  $\alpha_D 1^\circ 12'$  when freshly prepared, diminishing to  $\alpha_D 45'$  during 2 hours; the initial specific rotatory power therefore is  $[\alpha]_D + 30^\circ$ , becoming constant at  $[\alpha]_D + 18.7^\circ$ .

*Reduction with Zinc and Acetic Acid.*—Three grams were dissolved in 30 c.c. of warm alcohol, and treated with 5 grams of zinc dust followed by 1.5 grams of glacial acetic acid diluted with a few c.c. of alcohol; after 10 minutes, the liquid was filtered, and diluted largely



with water, which gave a voluminous precipitate. This product evidently is the zinc derivative of the regenerated dioxime, because when dry it weighed 5 grams, dissolved readily in alcohol, contained zinc, and gave  $[\alpha]_D + 78.3^\circ$  in a 1.5 per cent. solution in absolute alcohol. It was therefore dissolved in dilute aqueous caustic potash, and acidified with acetic acid, the precipitate thus obtained being recrystallised from ethyl acetate, which deposited the characteristic prisms of the  $\alpha$ -dioxime giving  $[\alpha]_D - 63.6^\circ$  in a 1.5 per cent. solution in absolute alcohol.

*Action of Benzoyl Chloride on isoNitrosocamphor.*

One hundred grams of *isonitrosocamphor* were dissolved in 500 c.c. of water containing 50 grams of sodium hydroxide; 100 grams of benzoyl chloride were then added in four portions, the liquid being cooled and well shaken after each addition.

The solid obtained in this manner was a mixture of a yellow substance with a white one, and weighed 100 grams. Extraction with 500 c.c. of boiling light petroleum removed almost the whole of the yellow constituent, and after digestion with a further quantity of 300 c.c., the colourless residue weighed 50 grams.

*Benzoyl Derivative of isoNitrosocamphor.*—The warm petroleum deposited bright yellow crystals, which were redissolved in the minimum quantity of hot alcohol, the solution being then cooled rapidly; the product was redissolved in hot petroleum, filtered from a small quantity of the colourless compound, and then recrystallised from alcohol until the melting point remained constant at  $105\text{--}106^\circ$ :

0.2035 gave 0.5347  $\text{CO}_2$  and 0.1258  $\text{H}_2\text{O}$ .  $\text{C} = 71.66$ ;  $\text{H} = 6.87$ .

0.4704 „ 21.4 c.c. nitrogen at  $20.5^\circ$  and 771 mm.  $\text{N} = 5.27$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$  requires  $\text{C} = 71.93$ ;  $\text{H} = 6.66$ ;  $\text{N} = 4.91$  per cent.

A solution containing 0.5006 gram in 25 c.c. of chloroform at  $21^\circ$  gave  $a_D 5^\circ 50'$  in a 2-dcm. tube, whence  $[\alpha]_D + 145.6^\circ$ .

The benzoyl derivative is readily soluble in ether, warm petroleum, and hot alcohol, and very readily in chloroform; it dissolves sparingly in cold petroleum, and is moderately soluble in cold alcohol, from which it crystallises in large, sulphur-yellow, transparent prisms. The solution in chloroform does not decolorise bromine.

*Hydrolysis.*—Forty-seven grams of the yellow benzoyl derivative were dissolved in absolute alcohol, and treated with 20 grams of potassium hydroxide in the minimum quantity of water. The red coloration immediately developed showed that hydrolysis takes place very readily, and after being heated during 1 hour, the liquid was evaporated to dryness, and the residue dissolved in water. On passing carbon dioxide through the liquid, *isonitrosocamphor* was precipitated

in pale yellow crystals, which, when recrystallised from boiling light petroleum, yielded colourless needles melting at 152—153°.

The isonitrosocamphor thus regenerated did not amount to more than 50 per cent. of the theoretical quantity, the remainder being converted probably into  $\alpha$ -camphornitrilic acid; on repeating with this specimen the benzylation as described above, the yellow and the colourless derivatives were obtained in approximately equal quantities.

*Action of Hydroxylamine.*—Attempts to prepare the monobenzoyl derivative of a camphordioxime by the action of hydroxylamine on the benzoyl derivative of isonitrosocamphor were unsuccessful. The yellow compound, when treated with the calculated amount of hydroxylamine hydrochloride in alcoholic solution, gave rise to an oily product from which a few crystals separated only after many days. In the presence of sodium acetate, introduced in concentrated aqueous solution, the reaction led to the production of the  $\alpha$ -dioxime of camphorquinone.

*The Colourless Benzoyl Derivative from isoNitrosocamphor.*—The residue left on removing yellow benzoylisonitrosocamphor from the crude product by means of boiling light petroleum, consisted of colourless, lustrous leaflets; after being recrystallised twice from hot alcohol, it melts at 136°:

0.1653 gave 0.4370  $\text{CO}_2$  and 0.0993  $\text{H}_2\text{O}$ .  $\text{C} = 72.10$ ;  $\text{H} = 6.67$ .

0.2813 „ 12.6 c.c. nitrogen at 19° and 769 mm.  $\text{N} = 5.21$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$  requires  $\text{C} = 71.93$ ;  $\text{H} = 6.66$ ;  $\text{N} = 4.91$  per cent.

A solution containing 1.0008 grams in 50 c.c. of chloroform at 20°, gave  $\alpha_D^{20} 5.6'$  in a 2-dcm. tube, whence  $[\alpha]_D + 127.4^\circ$ . The colourless benzoyl derivative is also distinguished from the yellow isomeride by its comparatively sparing solubility in organic media.

*Action of Light.*—It was noticed that a solution in chloroform, although quite colourless when freshly prepared, soon became yellow when exposed to light; moreover, liquids in which this change had occurred reddened litmus perceptibly after a few hours, whereas a solution prepared in dim light, and protected during several weeks, remained colourless and neutral.

The 2 per cent. solution giving  $[\alpha]_D + 127.4^\circ$  was accordingly divided into two portions, one of which was exposed to daylight, whilst the other was protected. After 2 days, the exposed solution had become pale yellow, and distinctly acid to litmus; the specific rotatory power diminished, becoming  $100^\circ$  in 10 days,  $69^\circ$  in 18 days,  $38^\circ$  in 40 days, and finally, after a period of 56 days, remaining constant at  $[\alpha]_D + 32^\circ$ . During this period, the liquid had become almost colourless, and was strongly acid towards litmus; on evaporating the chloroform, and treating the residue with sodium carbonate, benzoic



acid was removed, an oil remaining undissolved. This neutral substance is being investigated further.

The solution which had been protected from light had in the meanwhile undergone no change. The specific rotatory power remained unaltered during three months, after which period the liquid was still colourless, and only very feebly acid; on evaporating the chloroform, the original material was deposited, and after one crystallisation from alcohol melted at  $136^{\circ}$ .

*Hydrolysis of the Colourless Benzoyl Derivative.*—Fifty grams of the colourless benzoyl derivative were dissolved in 400 c.c. of boiling absolute alcohol, and the solution rapidly cooled. A concentrated aqueous solution of potassium hydroxide was then added in small quantities to the liquid, which was meanwhile cooled and agitated, because the action of the caustic potash developed a considerable amount of heat. The crystals suspended in the liquid rapidly dissolved, and each addition of alkali was accompanied by the development of an intense yellow coloration, which disappeared in a few seconds; the colour became fainter as the operation proceeded, until the liquid remained colourless on adding more caustic potash, this stage being reached when rather more than one molecular proportion of alkali had been employed. The liquid, when evaporated on the water-bath, left a residue, which, excepting a small quantity of ethyl benzoate, dissolved completely in a moderate amount of water, forming a solution which yielded a considerable proportion of a colourless oil on further dilution.

The product was shaken with ether, and the aqueous portion freed from ether on the water-bath; on saturating the cold liquid with carbon dioxide, no *isonitrosocamphor* was obtained, and dilute sulphuric acid was therefore added, yielding a colourless, crystalline precipitate, which weighed 35 grams, and consisted of benzoic and  $\alpha$ -camphornitrilic acids. An attempt to separate these compounds by means of the lead salts having failed, advantage was taken of the solubility of the first-named acid in warm light petroleum, which does not dissolve cyanolauronic acid very readily; 15 grams remained after three extractions with about 200 c.c. of the boiling solvent, and this residue was recrystallised, first from boiling water, then from dilute alcohol, in which it is very readily soluble. The specimen obtained in this way melted at  $149^{\circ}$ , and gave  $[\alpha]_D +73.2^{\circ}$  in a 2 per cent. chloroform solution:

0.1648 gave 0.3985  $\text{CO}_2$  and 0.1241  $\text{H}_2\text{O}$ .  $\text{C} = 65.95$ ;  $\text{H} = 8.36$ .

$\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{C} = 66.30$ ;  $\text{H} = 8.28$  per cent.

The ethereal extract was then evaporated, the oily residue dissolved in a small quantity of absolute alcohol, treated with a few grams of



potassium hydroxide in the minimum quantity of water, and after an interval of 12 hours, distilled in a current of steam. Eight grams of a colourless oil having a faint odour were thus obtained. The substance boils at  $277-278^{\circ}$  under 766 mm. pressure, has a sp. gr. 1.0121 at  $20^{\circ}$ , and  $[\alpha]_D +43.7^{\circ}$  at the same temperature; a 2 per cent. solution in chloroform gives  $[\alpha]_D +45.0^{\circ}$ :

0.1760 gave 0.4476  $\text{CO}_2$  and 0.1438  $\text{H}_2\text{O}$ .  $\text{C} = 69.36$ ;  $\text{H} = 9.08$ .

$\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C} = 68.90$ ;  $\text{H} = 9.09$  per cent.

From the fact that camphornitrilic acid is produced by the action of alcoholic potash, it is evident that this substance is the ethyl ester of that acid (compare Oddo, *Ber.*, 1895, 28, 1915).

#### *Action of Acetic Anhydride on isonitrosocamphor.*

Fifty grams of isonitrosocamphor were dissolved in 180 c.c. of water containing 14 grams of sodium hydroxide; acetic anhydride was then added in small quantities while the liquid was shaken and cooled. When the yellow colour of the sodium derivative had disappeared, a sufficient quantity of 10 per cent. sodium hydroxide solution was added to restore it, and the addition of acetic anhydride resumed. This alternating treatment with alkali and acetic anhydride was continued until the liquid, although alkaline, was no longer yellow; 30 grams of anhydride had then been added. A viscous oil, which was suspended in the solution, was extracted with ether as soon as the excess of acetic anhydride had been decomposed.

The aqueous solution was acidified with dilute hydrochloric acid giving a bulky precipitate of white, silky needles; this product, which weighed 9 grams, was camphornitrilic acid.

The viscous oil deposited on evaporating off the solvent from the dehydrated ethereal extract weighed 35 grams, and when left for several days in the desiccator became transformed into a paste of crystals. The solid product remaining undissolved by cold alcohol was found to consist of the anhydride of isonitrosocamphor, 5 grams being obtained in this manner.

The alcoholic filtrate from the anhydride, when heated with 11 grams of potassium hydroxide dissolved in the minimum quantity of water, yielded a deep red liquid; this was evaporated on the water-bath, the residue being treated with water and shaken with ether, which removed a small quantity of red oil. On passing a current of carbon dioxide through the aqueous liquid, 2 grams of isonitrosocamphor were precipitated, and the filtrate, when acidified with dilute hydrochloric acid, yielded a further quantity of camphornitrilic acid weighing 7 grams.

From this experiment, it appears that acetic anhydride converts *isonitrosocamphor* into a mixture of the true acetyl derivative and the *pseudo*-compound, a small proportion of the *isonitrosocamphor* undergoing conversion into the anhydride. The last-named is also formed in small quantities when acetic anhydride is added to the dried potassium derivative of *isonitrosocamphor* suspended in ether, but it is not produced when acetic anhydride acts on *isonitrosocamphor* in pyridine, the sole product being the oily mixture of acetyl derivatives.

*The Anhydride of isoNitrosocamphor.*

The pale yellow, crystalline substance obtained in small quantities when the dry alkali derivatives of *isonitrosocamphor* are treated with acyl chlorides or with acetic anhydride (see below), and formed in larger proportions when the last-named substance acts on a solution of the camphor derivative in aqueous sodium hydroxide, separates from alcohol in small, lustrous, yellow needles, and melts at  $187^{\circ}$  if the temperature is raised slowly; if the capillary tube is plunged in acid at  $150^{\circ}$ , and the temperature raised rapidly to  $190^{\circ}$ , fusion does not take place below  $194^{\circ}$ .

0.1648 gave 0.4236  $\text{CO}_2$  and 0.1315  $\text{H}_2\text{O}$ .  $\text{C} = 70.10$ ;  $\text{H} = 8.86$ .

0.3946 „ 29.2 c.c. nitrogen at  $22^{\circ}$  and 765 mm.  $\text{N} = 8.43$ .

$\text{C}_{20}\text{H}_{28}\text{O}_3\text{N}_2$  requires  $\text{C} = 69.77$ ;  $\text{H} = 8.14$ ;  $\text{N} = 8.14$  per cent.

0.5044 gram in 25 c.c. of chloroform at  $21^{\circ}$  gave  $\alpha_D$   $5^{\circ}43'$  in a 2-dcm. tube, whence  $[\alpha]_D + 141.7^{\circ}$ . A determination of the molecular weight in benzene gave the following result:

*Molecular Weight of  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ , 181;  $\text{C}_{20}\text{H}_{28}\text{O}_3\text{N}_2$ , 344.*

| Grams of benzene. | Grams of substance. | Grams of substance in 100 grams of benzene. | Depression of the freezing point. | Molecular weight deduced. |
|-------------------|---------------------|---|-----------------------------------|---------------------------|
| 17.439            | 0.2857              | 1.639                                       | 0.254°                            | 329                       |
| „                 | 0.5885              | 3.375                                       | 0.534                             | 322                       |
| „                 | 0.8899              | 5.103                                       | 0.810                             | 321                       |

The substance does not yield hydrogen bromide when heated with bromine; it acts vigorously with concentrated sulphuric acid, forming a solution which remains clear on dilution. On hydrolysis with alcoholic potash, it yields camphornitrilic acid, no *isonitrosocamphor* being regenerated.

Although the anhydride has been obtained in a variety of ways, the yield is always very small, the following process, although far from satisfactory, being the most convenient. Twenty grams of yellow benzoylisonitrosocamphor are dissolved in 200 c.c. of dried benzene and heated on the water-bath with 25 grams of the finely-powdered potassium derivative, the contents of the flask being frequently shaken; the red colour of the alkali derivative soon disappears, the liquid becoming filled with potassium benzoate in the form of a colourless, gelatinous precipitate which becomes granular on continued boiling; after 3 hours, the product is shaken with water, the benzene being then dried with calcium chloride and evaporated. The yellow residue soon hardens, and, when moistened with alcohol and drained on earthenware, yields about 18.5 grams of the anhydride. It is noteworthy that the sodium derivative of isonitrosocamphor, when heated with the benzoyl derivative under similar conditions, does not yield the anhydride.

*Transformation of the Anhydride on Fusion.*—When the anhydride is melted in a capillary tube, there appears to be an evolution of gas; if, however, a few decigrams are heated in a test-tube to a temperature slightly above the melting point, no definite effervescence is observed, the greater part of the substance being converted into a colourless liquid which soon solidifies to a hard, sparingly soluble product; a small proportion of a volatile, pleasant-smelling liquid, which accompanies the solid, no doubt causes the fused anhydride, when in a narrow tube, to appear to liberate gas.

The solid thus obtained was drained on earthenware, and recrystallised twice from alcohol, which deposited colourless crystals melting at  $176^{\circ}$ :

0.2409 gave 17.5 c.c. nitrogen at  $17^{\circ}$  and 772 mm.  $N = 8.56$ .

$C_{20}H_{25}O_3N_2$  requires  $N = 8.14$  per cent.

0.2951 gram in 25 c.c. of chloroform at  $20^{\circ}$  gave  $\alpha_D 1^{\circ}17'$  in a 2-dm. tube, whence  $[\alpha]_D +54.3^{\circ}$ . Hydrolysis with alcoholic potash resolves the substance into camphornitrilic acid; and it is therefore probably the anhydride of that acid, obtained by Oddo and Leonardi from isonitrosocamphor and acetic anhydride or acetyl chloride (*Gazzetta*, 1896, 26, i, 405), although the melting point given by these authors is  $172-173^{\circ}$  (compare Haller and Minguin, *Compt. rend.*, 1896, 123, 216).



*Oxidation of isoNitrosocamphor with Potassium Ferricyanide.*

The conversion of *isonitrosocamphor* into the anhydride under the influence of mild dehydrating agents suggested the possibility of its resembling the dioximes, and yielding a peroxide when treated with a suitable oxidising agent. This would be a product of some interest, because on reduction it might give rise to the stereoisomeric *isonitrosocamphor* in place of the well-known modification. On oxidising it in alkaline solution with potassium ferricyanide, however, a quantitative yield of  $\alpha$ -nitrocamphor is obtained, although the formation of a colourless precipitate on mixing the materials seems to indicate that the peroxide represents an intermediate stage in the oxidation.

Ten grams of *isonitrosocamphor* were dissolved in 100 c.c. of water containing 15 grams of potassium hydroxide; a solution of 25 grams of potassium ferricyanide in 100 c.c. of water was then added, when a bulky, colourless precipitate was formed. In the course of a few minutes, this substance disappeared, and after an interval of 1 hour the clear, deep-brown solution was acidified with dilute hydrochloric acid. The yellow, crystalline precipitate thus obtained consisted of  $\alpha$ -nitrocamphor, and when recrystallised from petroleum melted at 103°.

*Action of Acyl Chlorides on the Alkali Derivatives of isoNitrosocamphor.*

The sodium derivative of *isonitrosocamphor*, prepared by dissolving 100 grams in 100 c.c. of water containing 25 grams of sodium hydroxide, and adding to the clear, pale-red solution 50 grams of the alkali dissolved in the minimum quantity of hot water, separated from the liquid, on cooling, in lustrous, yellow spangles. The potassium derivative produced in the same way crystallised from the hot, alkaline liquid in lustrous, red leaflets. Both substances dissolve very readily in water and in absolute alcohol, but are insoluble in ether.

*Action of Acetyl Chloride.*—The finely powdered sodium derivative was suspended in ether containing calcium chloride, cooled in melting ice, and treated with acetyl chloride also dissolved in ether, until the yellow particles had disappeared. The insoluble products were filtered, washed several times with ether, then treated with water, and finally washed with a small quantity of ether on the filter pump; on recrystallising from hot alcohol, lustrous, pale yellow needles melting at 187° were obtained. The ethereal solution, on evaporation, deposited a pale yellow, viscous oil which did not crystallise after several weeks

in a desiccator. The yellow solid consisted of the anhydride of *isonitrosocamphor*, whilst the viscous oil, which yielded *camphornitrilic acid* and *isonitrosocamphor* on hydrolysis, was probably a mixture of acetyl *isonitrosocamphor* and the corresponding *pseudo-derivative*.

*Action of Benzoyl Chloride.*—The behaviour of sodium *isonitrosocamphor* and the corresponding potassium derivative towards benzoyl chloride was studied under the conditions just prescribed for acetyl chloride, action being much slower than in the case of the latter; a small proportion of the anhydride was isolated, but neither the colourless nor the yellow benzoyl derivative of *isonitrosocamphor* was detected in the product.

*Action of Phosphorus Oxychloride.*—The dried potassium derivative was suspended in ether and treated with a dilute ethereal solution of phosphorus oxychloride; action was vigorous, causing the solvent to boil, and when the red colour of the alkali compound had disappeared, the pale yellow solution was filtered. From this liquid, which deposited an oil on evaporation, a small quantity of anhydride was obtained, whilst the product insoluble in ether, when dissolved in water and acidified, yielded *camphornitrilic acid*.

*Action of m-Nitrobenzoyl Chloride on  
isonitrosocamphor.*

Fifty grams of *isonitrosocamphor* were dissolved in 400 c.c. of water containing 25 grams of sodium hydroxide; 50 grams of *m*-nitrobenzoyl chloride were then added to the liquid, which was cooled and shaken vigorously until the oily product had become granular. The filtered product was crushed, and steeped in dilute caustic alkali, being afterwards dried, and extracted with 400 c.c. of boiling alcohol; the filtered liquid deposited 30 grams of minute yellow needles, and left 5 grams of colourless powder undissolved.

The yellow product was recrystallised from alcohol until the melting point was constant, forming small, pale yellow, lustrous needles, melting at 136—137°:

0.1919 gave 15.3 c.c. nitrogen at 20° and 743 mm.  $N = 8.90$ .

$C_{17}H_{15}O_5N_2$  requires  $N = 8.48$  per cent.

0.5057 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D^{20} 5.12'$  in a 2-dm. tube, whence  $[\alpha]_D^{20} + 128.5^\circ$ .

The substance is insoluble in boiling water, and not very soluble in cold alcohol, although dissolving readily on boiling; it is also readily soluble in ethyl acetate, benzene, and glacial acetic acid, and very

readily in chloroform. It is sparingly soluble in boiling petroleum, from which it crystallises in minute needles.

The colourless, slightly soluble *m*-nitrobenzoyl derivative which remained undissolved by the boiling alcohol, was dissolved in 250 c.c. of boiling ethyl acetate, which deposited long, lustrous, rectangular leaflets melting at 152°:

0.2189 gave 15.8 c.c. nitrogen at 16° and 759 mm.  $N = 8.40$ .

$C_{17}H_{18}O_5N_2$  requires  $N = 8.48$  per cent.

The substance is readily soluble in chloroform, and moderately soluble in boiling acetone, from which it crystallises in transparent, hexagonal plates; it dissolves sparingly in boiling alcohol, and is practically insoluble in petroleum.

A solution containing 0.5236 gram in 25 c.c. of chloroform at 20° gave  $\alpha_D 4.45'$  in a 2-dcm. tube, whence  $[\alpha]_D + 113.4^\circ$ ; on leaving this liquid exposed to light, it behaved like the colourless benzoyl derivative of *isonitrosocamphor*, becoming yellow and acid. During 8 days, the specific rotatory power fell to  $[\alpha]_D + 53^\circ$ , and ultimately remained constant at  $[\alpha]_D + 32^\circ$ .

#### *A Stereoisomeric isoNitrosocamphor.*

Considering the behaviour of the yellow and the colourless benzoyl derivatives of *isonitrosocamphor* towards alcoholic potash, it was to be expected that the corresponding *m*-nitrobenzoyl derivatives would yield *isonitrosocamphor* and  $\alpha$ -camphornitrilic acids respectively, mixed in each case with *m*-nitrobenzoic acid. The results of the two hydrolyses are not, however, comparable, and although a complete account of the changes which take place must be postponed, sufficient progress has been made to justify the description of an interesting substance having properties which lead to the conclusion that it is a stereoisomeric *isonitrosocamphor*.

When small quantities of the yellow *m*-nitrobenzoyl derivative just described are dissolved in alcohol and treated with excess of concentrated potassium hydroxide, a red coloration is immediately developed, and on evaporating the liquid, a very dark red residue remains. On dissolving this in a few c.c. of water, and passing carbon dioxide through the liquid, a bulky precipitate is soon formed, and if this is filtered at the pump, drained on earthenware, and dried in a desiccator, hot light petroleum extracts a substance which is more readily soluble than ordinary *isonitrosocamphor*, and crystallises in lustrous leaflets melting at 114°; if the temperature is carried to 130–140°, the liquid solidifies, and melts again at 152–153°, the product being indistinguishable from ordinary *isonitrosocamphor*.



When dissolved in glacial acetic acid and treated with sodium nitrite, the new substance yields camphorquinone.

A solution containing 0.2169 gram in 20 c.c. of chloroform at 20° gave  $\alpha_D$  3°45' in a 2-dm. tube when examined immediately after preparation, whence  $[\alpha]_D +172.9^\circ$ ; this specific rotatory power gradually increased, however, until after 3 days it became constant at  $[\alpha]_D +195.9^\circ$ .

The substance, like isonitrosocamphor, gives no coloration with ethereal ferric chloride. It develops an intense yellow coloration with caustic alkalis, and on adding a dilute solution of ferrous sulphate to the yellow liquid, the characteristic, dark blue precipitate is formed as in the case of the ordinary modification.

The conditions under which the new substance is obtainable are being further investigated, because it was found that if hydrolysis is carried out with only theoretical amounts of caustic potash, the isonitrosocamphor recovered consisted chiefly of the common form. Twenty grams of the *m*-nitrobenzoyl derivative treated in this way yielded 9 grams of isonitrosocamphor, from which boiling light petroleum extracted a mixture of snow-white leaflets and needles; the product began to shrink at 125°, melted indefinitely at 140—150°, and gave  $[\alpha]_D +192.1^\circ$  in a 1.5 per cent. chloroform solution, rising to 195°. This is the only occasion on which the new modification has been obtained quite colourless. When prepared in the manner indicated above, it is invariably stained with red, and a specimen has been recrystallised four times from light petroleum without becoming colourless; the ultimate shade of red was certainly paler, and the melting point remained at 114°. When the unstable isonitrosocamphor is mixed with the better known modification, the melting point is indefinite, and, unlike a mixture of dissimilar substances, the product melts above 114° or below 152°, according to the form which preponderates.

Reference to the paper of Claisen and Manasse (*Annalen*, 1893, 274, 71) shows that these investigators suspected the existence of a more fusible, unstable isomeride, they having experienced great difficulty in raising the melting point of ordinary isonitrosocamphor by recrystallisation. I am able to confirm their observations on this point, and have found that a specimen, which, after crystallisation from water, melted indefinitely at 140—145°, and gave  $[\alpha]_D +191.2^\circ$ , could be obtained in long, slender, colourless needles melting at 152—153°, and giving  $[\alpha]_D +196.6^\circ$ , by heating it during a few minutes at 150°, and recrystallising the product from boiling light petroleum. This may be taken as the specific rotatory power of isonitrosocamphor, and not  $[\alpha]_D +221.9^\circ$  (Forster, *Proc.*, 1902, 18, 238).

In view of the preceding results, the hydrolysis of the yellow benzoyl derivative of *isonitrosocamphor* was repeated under comparable conditions, but the course of the reaction was identical with that previously described (p. 526).

*Action of Chloroacetic Acid on isoNitrosocamphor.*

Whilst benzoyl and *m*-nitrobenzoyl chlorides have each furnished a yellow and a colourless acyl derivative, chloroacetic acid, under the conditions described below, has given rise to one substance only; this is colourless, and does not yield *isonitrosocamphor* on hydrolysis.

Fifty grams of *isonitrosocamphor* and 25 grams of chloroacetic acid were dissolved in 250 c.c. of absolute alcohol, and treated with 21 grams of sodium hydroxide in the minimum quantity of water; a vigorous action ensued, and when this had subsided, the liquid was heated during half an hour on the water-bath, and then evaporated. The residue was dissolved in water and acidified with dilute hydrochloric acid, which precipitated a viscous oil; this was washed twice with water, dissolved in sodium carbonate, and extracted with ether in order to remove a small quantity of deep red oil, the colourless liquid being ultimately freed from ether and acidified. The semi-solid product, when treated with a small quantity of cold alcohol, yielded 15 grams of a substance which, after further purification, crystallised from boiling water in colourless, lustrous needles melting at  $163^{\circ}$  :

0.1064 gave 0.2366  $\text{CO}_2$  and 0.0696  $\text{H}_2\text{O}$ .  $\text{C} = 60.62$  ;  $\text{H} = 7.26$ .

0.3037 „ 15.3 c.c. nitrogen at  $17^{\circ}$  and 768 mm.  $\text{N} = 5.91$ .

$\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$  requires  $\text{C} = 60.25$  ;  $\text{H} = 7.11$  ;  $\text{N} = 5.85$  per cent.

0.5946 gram in 20 c.c. of chloroform at  $20^{\circ}$  gave  $\alpha_D$   $8^{\circ}36'$  in a 2-dcm. tube, whence  $[\alpha]_D + 144.6^{\circ}$ .

The substance dissolves in sodium carbonate solution, and although readily soluble in organic media generally, it is practically insoluble in petroleum.

My thanks are again due to Miss F. M. G. Micklethwait for carrying out the analytical operations required in this investigation.

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LIX.—*Studies in the Camphane Series. Part XII.*  
*aa-Benzoylnitrocamphors and aa-Benzoyliodo-*  
*camphor.*

By MARTIN ONSLOW FORSTER and ERNEST ARTHUR JENKINSON, A.R.C.S.

HAVING obtained two stereoisomeric  $\alpha$ -derivatives from benzoylcamphor and *m*-nitrobenzoylcamphor containing chlorine and bromine substituents (Trans., 1902, 81, 160 and 406), it appeared desirable to ascertain whether benzoylnitrocamphor and benzoyliodocamphor could also be produced in two modifications.

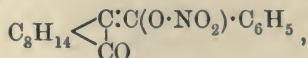
On treating with nitric acid a solution of benzoylcamphor in glacial acetic acid, a crystalline derivative separates from the liquid, which subsequently yields an isomeric substance when diluted with water. In most of their relationships, these compounds resemble the analogous benzoylchlorocamphors and benzoylbromocamphors. They are neutral substances, and give no coloration with ferric chloride. The more soluble one melts at  $110^{\circ}$ , and yields a readily soluble *m*-nitro-derivative melting at  $112$ – $113^{\circ}$ ; the isomeric benzoylnitrocamphor, which dissolves sparingly in common media, melts at  $225^{\circ}$ , and gives rise to a *m*-nitro-derivative melting at  $175^{\circ}$ . When hydrolysed with alcoholic potash, both modifications yield benzoic acid and  $\alpha'$ -nitrocamphor, which, in the case of their nitro-derivatives, is associated with *m*-nitrobenzoic acid. Concentrated sulphuric acid also liberates benzoic acid and *m*-nitrobenzoic acids from the respective pairs.

The specific rotatory power of the benzoylnitrocamphors is, however, a very puzzling feature of the substances, as appears from the following table:—

|   | $[\alpha]_D$ in<br>chloroform. | M. p.         |
|---|--------------------------------|---------------|
| $\alpha'$ -Benzoyl- $\alpha$ -chlorocamphor ..... | $-28^{\circ}$                  | $88^{\circ}$  |
| <i>m</i> -Nitro-derivative .....                  | $+40$                          | $72$ – $74$   |
| $\alpha$ -Benzoyl- $\alpha'$ -chlorocamphor ..... | $+26$                          | $219$         |
| <i>m</i> -Nitro-derivative .....                  | $+7$                           | $110$         |
| $\alpha'$ -Benzoyl- $\alpha$ -bromocamphor .....  | $+10$                          | $114$         |
| <i>m</i> -Nitro-derivative .....                  | $+88$                          | $93$ – $94$   |
| $\alpha$ -Benzoyl- $\alpha'$ -bromocamphor .....  | $-19$                          | $214$         |
| <i>m</i> -Nitro-derivative .....                  | $-26$                          | $101$ – $102$ |
| $\alpha'$ -Benzoyl- $\alpha$ -nitrocamphor .....  | $+163$                         | $110$         |
| <i>m</i> -Nitro-derivative .....                  | $+176$                         | $112$ – $113$ |
| $\alpha$ -Benzoyl- $\alpha'$ -nitrocamphor .....  | $+245$                         | $225$         |
| <i>m</i> -Nitro-derivative .....                  | $+178$                         | $175$         |
| $\alpha'$ -Benzoyl- $\alpha$ -iodocamphor .....   | $+48$                          | $136$         |



Comparing  $\alpha$ -benzoylcamphor, having  $[\alpha]_D + 125^\circ$  in chloroform with  $\alpha'$ -nitrocamphor, which has  $[\alpha]_D - 124^\circ$  in benzene, we expected to find that the optical activity of  $\alpha$ -benzoyl- $\alpha'$ -nitrocamphor would be very feeble, in view of the results obtained by Lowry with the chloronitrocamphors and bromonitrocamphors, and of the experiments made with substituted benzoylcamphors to which reference has been made. In any case, it seemed unlikely that the specific rotatory power of  $\alpha$ -benzoyl- $\alpha'$ -nitrocamphor would greatly exceed  $+100^\circ$  in chloroform, considering that  $\alpha'$ -nitrocamphor has  $[\alpha]_D - 27^\circ$  in that solvent. It is therefore surprising that the specific rotatory power is  $[\alpha]_D + 245^\circ$ , whilst the isomeride, which, for the reason just indicated, should have  $[\alpha]_D$  lying between  $-100^\circ$  and  $0^\circ$ , has  $[\alpha]_D + 163^\circ$ . We are compelled to leave this abnormality unexplained for the present. It has been suggested that a nitric ester of enolic benzoylcamphor,

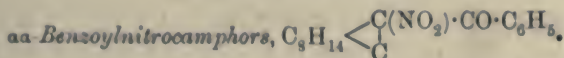


which would be isomeric with  $\alpha\alpha$ -benzoylnitrocamphor, might have a high rotatory power, but the occurrence of two modifications, the indifference of these towards bromine, and the production of  $\alpha'$ -nitrocamphor under the influence of alcoholic potash, seems to preclude such a formula for either of the substances derived from benzoylcamphor.

Although the more fusible benzoylbromocamphor can be transformed into the isomeride by the agency of hydrogen bromide, we have found that the corresponding benzoylnitrocamphor resembles the chloro-derivative, and remains unchanged.

Benzoyliodocamphor is produced when iodine, dissolved in potassium iodide, is added to a solution of enolic benzoylcamphor in caustic potash. It is a pale yellow substance which melts at  $136^\circ$ , and is quite stable in the solid condition, although solutions rapidly turn brown. The alternative method of preparing benzoylchloro- and benzoylbromocamphors, namely by treating the camphor derivative dissolved in acetic acid with the halogen in the same medium, is not applicable in this case, nor have we succeeded in transforming benzoyliodocamphor into a less fusible, and comparatively insoluble, modification; hydrogen bromide has no action on the substance, and hydrogen iodide merely reduces it. The specific rotatory power of benzoyliodocamphor is  $[\alpha]_D + 47.7^\circ$ , and as iodocamphor has  $[\alpha]_D + 160^\circ$ , we regard the new derivative as  $\alpha'$ -benzoyl- $\alpha$ -iodocamphor.

## EXPERIMENTAL.



When benzoylcamphor is dissolved in fuming nitric acid, a very vigorous action takes place spontaneously, but the product cannot be made to yield a crystalline substance. If nitration is carried out in glacial acetic acid, however, two isomeric substances are obtained in proportions which may be varied at will.

Enolic benzoylcamphor in quantities of 5 grams was placed in a series of small beakers, and dissolved in 50 c.c. of glacial acetic acid. While the solution was still warm, 1.5 c.c. of fuming nitric acid was added to the contents of each beaker, which became hot, and evolved brown fumes. As the liquid cooled, small, rectangular plates crystallised, and after an interval these were filtered, the filtrate being diluted largely with water, which precipitated a colourless solid. Under these conditions, 25 grams of benzoylcamphor furnished 7.5 grams of the sparingly soluble product and 10.5 grams of the isomeride, but if a stronger solution of benzoylcamphor is employed, or if a greater proportion of nitric acid is added, the yield of the readily soluble product is very greatly diminished.

*α'-Benzoyl-α-nitrocamphor* was obtained from the colourless solid precipitated by water from the acetic acid filtrate. Fifteen grams were treated with 100 c.c. of 75 per cent. acetic acid and filtered, the filtrate being rejected. The residue was extracted twice with 100 c.c. of cold glacial acetic acid, these extracts being diluted largely with water; a white, flocculent precipitate was obtained in each case, and these, when recrystallised from boiling alcohol, melted at 110°.

0.1565 gave 0.3880  $CO_2$  and 0.0934  $H_2O$ . C = 67.61; H = 6.63.

0.2179 „ 9.0 c.c. of nitrogen at 23° and 766 mm. N = 4.70.

$C_{17}H_{19}O_4N$  requires C = 67.77; H = 6.31; N = 4.65 per cent.

The substance is very readily soluble in chloroform, glacial acetic acid, and boiling alcohol, crystallising from the last-named in long, white needles; less concentrated alcoholic solutions deposit it in well-formed prisms.

A solution containing 0.5010 gram in 25 c.c. of chloroform at 25° gave  $\alpha_D$  6°32' in a 2-dcm. tube, whence  $[\alpha]_D + 163.0^\circ$ .

This compound is insoluble in caustic alkalis, and does not give Liebermann's reaction; it may be heated with boiling bromine in the presence of iron without evolving hydrogen bromide. Unlike the corresponding benzoylbromocamphor, *α'-benzoyl-α-nitrocamphor* is not transformed into the isomeride by fuming hydrobromic acid.

*α-Benzoyl-α'-nitrocamphor* is the substance which crystallises in rectangular plates as the acetic acid cools.

0.1476 gave 0.3688 CO<sub>2</sub> and 0.0868 H<sub>2</sub>O. C = 68.14; H = 6.53.

0.2506 „ 10.0 c.c. nitrogen at 17° and 764 mm. N = 4.66.

C<sub>17</sub>H<sub>19</sub>O<sub>4</sub>N requires C = 67.77; H = 6.31; N = 4.65 per cent.

A solution containing 0.4996 gram in 25 c.c. of chloroform at 20° gave α<sub>D</sub> 9°48' in a 2-dcm. tube, whence [α]<sub>D</sub> +245.2°.

The substance is characterised by sparing solubility in ordinary solvents, 1 gram requiring 50 c.c. of boiling alcohol, which deposits it in colourless, rectangular plates melting at 225° and evolving gas. It is moderately soluble in boiling ethyl acetate, glacial acetic acid, acetone, and benzene, but dissolves very sparingly in the cold liquids; from the two first named, it separates in the same form as from alcohol, but acetone deposits it in clear-cut, hexagonal prisms, whilst from benzene it crystallises in a felted mass of long, silky needles. It is insoluble in cold petroleum, and dissolves very sparingly in the boiling liquid, from which it separates in minute needles; cold chloroform, however, dissolves it in moderate quantity.

*α-Benzoyl-α'-nitrocamphor* is insoluble in caustic alkalis, does not give Liebermann's reaction, and is indifferent towards bromine. Attempts to reduce it with zinc dust and acetic acid were unsuccessful, but aluminium amalgam in a hot dilute alcoholic solution furnished a liquid which reduced ammoniacal silver nitrate, although no definite hydroxylamino-derivative could be isolated.

#### *Action of Alcoholic Potassium Hydroxide on Benzoylnitrocamphor.*

Five grams of benzoylnitrocamphor were dissolved in 300 c.c. of absolute alcohol and heated with 2.5 grams of potassium hydroxide during 2—3 hours. The residue obtained on evaporating the alcohol was completely soluble in water, and gave no precipitate when saturated with carbon dioxide; had the substance been a nitric ester, enolic benzoylcamphor would have been precipitated at this stage. On adding dilute hydrochloric acid to the aqueous liquid, a crystalline precipitate was formed, and this was filtered, washed and dried; it was then heated at 100° during several hours. The product was extracted with sodium carbonate, which dissolved the benzoic acid, the residue being treated with a small quantity of alcohol and drained on earthenware, leaving a pale yellow solid, which, after crystallisation from alcohol melted at 193°, evolving gas and becoming yellow; it was identified as the anhydride of pseudonitrocamphor (Lowry, Trans., 1898, 73, 996).



*aa-m-Nitrobenzoylnitrocamphors*,  $C_8H_{14} \begin{matrix} \diagup C(NO_2) \cdot CO \cdot C_6H_4 \cdot NO_2 \\ \diagdown CO \end{matrix}$ .

The benzoylnitrocamphors, in quantities of 5 grams, were dissolved in 25 c.c. of fuming nitric acid (sp. gr. 1.50), a slight rise of temperature occurring in each case. When cold, the liquid was poured into water, which precipitated the nitrobenzoyl derivatives. The product from the benzoylnitrocamphor which melts at  $110^\circ$  being somewhat pasty, even after continued washing, it was extracted with a small quantity of boiling alcohol before being crystallised; the isomeride, on the other hand, was obtained in a granular condition on precipitation with water.

*a'-m-Nitrobenzoyl-a-nitrocamphor* is moderately soluble in boiling petroleum ether, from which it crystallises in transparent, rhomboidal plates on cooling; it melts at  $112-113^\circ$ :

0.3366 gave 23.6 c.c. nitrogen at  $18^\circ$  and 771 mm.  $N = 8.22$ .

$C_{17}H_{18}O_6N_2$  requires  $N = 8.09$  per cent.

A solution containing 0.5005 gram dissolved in 25 c.c. of chloroform at  $20^\circ$  gave  $\alpha_D 7^\circ 2'$  in a 2-dcm. tube, whence  $[\alpha]_D + 175.6^\circ$ .

The substance is very readily soluble in chloroform, ether, benzene, and ethyl acetate; it is insoluble in cold petroleum, and is dissolved in only moderate quantities by methyl and ethyl alcohols.

*a-m-Nitrobenzoyl-a'-nitrocamphor* is sparingly soluble in boiling alcohol, from which it crystallises in lustrous, rectangular, straw-yellow prisms; it melts and evolves gas at  $175^\circ$ :

0.1566 gave 11.6 c.c. nitrogen at  $17^\circ$  and 746 mm.  $N = 8.44$ .

$C_{17}H_{18}O_6N_2$  requires  $N = 8.09$  per cent.

A solution containing 0.5000 gram dissolved in 25 c.c. of chloroform at  $20^\circ$  gave  $\alpha_D 7^\circ 7.5'$  in a 2-dcm. tube, whence  $[\alpha]_D + 178.1^\circ$ .

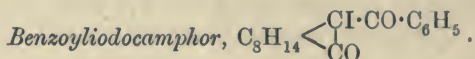
It is much less readily soluble than the isomeric substance, dissolving sparingly in ethyl acetate, glacial acetic acid, and boiling petroleum; it is scarcely soluble in cold alcohol, but dissolves readily in hot benzene, from which it crystallises in transparent, rectangular plates.

When heated with alcoholic potash under the conditions prescribed for benzoylnitrocamphor, *m*-nitrobenzoic acid and *a*-nitrocamphor were obtained.

*Action of Concentrated Sulphuric Acid on the Benzoylnitrocamphors and their m-Nitro-derivatives.*

When  $\alpha$ -benzoyl- $\alpha'$ -nitrocamphor is dissolved in concentrated sulphuric acid, the liquid becomes warm and pale yellow, and if poured on crushed ice yields a snow-white precipitate of benzoic acid. In the case of the isomeride, the solution becomes hot and deep yellow, yielding benzoic acid on dilution. In neither case could the camphor residue be traced, as it probably undergoes sulphonation.

When the *m*-nitrobenzoylnitrocamphors were treated with concentrated sulphuric acid in the same way, the product obtained on adding the liquid to crushed ice remained semi-solid during several days. When quite hard, the powdered product was extracted with sodium carbonate, which dissolved *m*-nitrobenzoic acid, leaving in each case a small quantity of a neutral, nitrogenous compound, which has not been identified.



Twenty grams of enolic benzoylcamphor were dissolved in aqueous potassium hydroxide ( $1\frac{1}{2}$  mols.), and slowly treated with a solution of 30 grams of iodine ( $1\frac{1}{2}$  mols.) in 100 c.c. of aqueous potassium iodide. The iodine solution was added in small quantities to the well-stirred liquid, when the halogen was immediately decolorised, brown, sticky clots being produced; the product gradually hardened, and when granular, was filtered, digested with a small quantity of cold alcohol, and washed without delay until the excess of iodine had been removed. The substance, when twice crystallised from alcohol, deposited lustrous, straw-yellow plates, melting to a pale-brown liquid at  $136^\circ$ :

0.1877 gave 0.1137 AgI.  $I = 32.73$ .

$C_{17}H_{19}O_2I$  requires  $I = 33.24$  per cent.

A solution containing 0.5024 gram dissolved in 25 c.c. of chloroform at  $21^\circ$  gave  $\alpha_D$   $1^\circ 55'$  in a 2-dm. tube, whence  $[\alpha]_D + 47.7^\circ$ .

Benzoyliodocamphor is readily soluble in acetone, chloroform, and ethyl acetate; it is moderately soluble in alcohol, glacial acetic acid, and boiling petroleum, separating from the last-named in transparent, hexagonal plates. Although the purified substance is quite stable in the dry condition, it slowly darkens when exposed to sunlight, and solutions undergo a complete change; a freshly prepared solution in petroleum ether, for example, is slightly yellow, but soon becomes pink, and ultimately deep violet, whilst an alcoholic solution becomes dark brown. Recrystallisation of benzoyliodocamphor, therefore, must be carried out as quickly as possible.

It was hoped that the iodine atom in benzoyliodocamphor would prove sufficiently reactive to undergo exchange for the cyanogen group. The compound undergoes no change when heated in benzene with silver cyanide during several days, however, and on warming it with alcoholic potassium cyanide, enolic benzoylcamphor is regenerated. Benzoylbromocamphor behaves like the iodine derivative, whilst benzoylchlorocamphor remains unchanged. An attempt to prepare benzoylcyanocamphor by passing cyanogen into a solution of enolic benzoylcamphor in aqueous potash was also unsuccessful.

Boiling pyridine has no action on benzoyliodocamphor, but the latter is sensitive towards oxidising agents. Cold fuming nitric acid liberates iodine; and concentrated nitric acid, although without action at first, sets free the halogen on warming. Iodine is slowly removed by boiling aqueous potassium iodide, whilst the alcoholic solution of benzoyliodocamphor, when treated with ethereal ferric chloride, develops a pale green coloration which becomes more intense and then bluish, the final tint resembling that of a dilute solution of benzoylcamphor with ferric chloride. Alcoholic silver nitrate has no action on the substance until boiled, when precipitation of silver iodide takes place slowly; moist silver oxide, when heated with benzoyliodocamphor dissolved in alcohol, undergoes reduction without converting it into any definite substance.

On passing chlorine into a cold solution of benzoyliodocamphor in dry chloroform, the iodine becomes replaced by chlorine, and  $\alpha'$ -benzoyl- $\alpha$ -chlorocamphor can be isolated from the product. The production of this substance in the manner indicated, taken in conjunction with the low melting point, seems to indicate that the iodo-derivative is the  $\alpha'$ -benzoyl- $\alpha$ -iodocamphor.

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## LX.—*The Composition of Caro's Acid.*

By THOMAS SLATER PRICE, D.Sc.

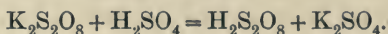
THE various experiments undertaken to determine the composition of Caro's acid (Baeyer and Villiger, *Ber.*, 1901, 34, 853; Lowry and West, *Trans.*, 1900, 77, 950; Price, *Ber.*, 1902, 35, 292; Armstrong and Lowry, *Proc. Roy. Soc.*, 1902, 70, 94) lead to the conclusion that the composition of the undiluted acid probably differs from that substance in solution. In the former case, it is probably  $\text{H}_2\text{S}_4\text{O}_{14}$ .



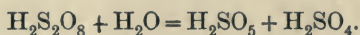
(Lowry and West, *loc. cit.*), whereas in the latter case the composition is represented either by  $\text{H}_2\text{SO}_5$  or by  $\text{H}_2\text{S}_2\text{O}_9$ .

Since my former results are not in accordance with the formula  $\text{H}_2\text{S}_2\text{O}_9$  (Armstrong and Lowry, *loc. cit.*), I have therefore deemed it necessary to make further experiments, although the method employed is not as accurate as that of these authors. The method I used to decide between the two formulæ  $\text{H}_2\text{SO}_5$  and  $\text{H}_2\text{S}_4\text{O}_{14}$  is based on the following considerations. The formation of Caro's acid from potassium persulphate and concentrated sulphuric acid can be represented by the following equations:

(1) If the formula is  $\text{H}_2\text{SO}_5$ , we have

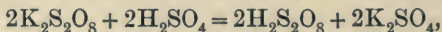


The  $\text{H}_2\text{S}_2\text{O}_8$  is then hydrolysed by the water present according to the equation:



For every molecule of Caro's acid formed, the acidity (expressed in grams  $\text{H}_2\text{SO}_4$ , since  $\text{H}_2\text{SO}_5$  has the same titre as  $\text{H}_2\text{SO}_4$ ) will increase by an equivalent amount, in this case by 1 molecule.

(2) For the formula  $\text{H}_2\text{S}_4\text{O}_{14}$  the first equation would be

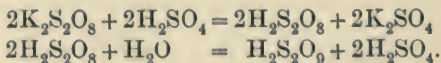


the  $\text{H}_2\text{S}_2\text{O}_8$  then splitting up into hydrogen peroxide and Caro's acid,



so that for every molecule of Caro's acid formed there must also result 1 molecule of hydrogen peroxide.\* If hypothesis (1) is true, then the ratio (a) of iodine value to increase of acidity (expressed as  $\text{H}_2\text{SO}_4$ ) should have the value 2.59. According to the formula  $\text{H}_2\text{S}_4\text{O}_{14}$ , the ratio (b) of the iodine value to the amount of hydrogen peroxide formed should be 7.47. The results formerly obtained (*Ber.*, 1902, 35, 294) gave 2.56 as the mean value of (a), whereas (b) varied between 136.0 and 566.7; therefore the formula should be  $\text{H}_2\text{SO}_5$ .

Armstrong and Lowry (*loc. cit.*) have shown that in all probability the formula is either  $\text{H}_2\text{S}_2\text{O}_9$  ( $2\text{H}_2\text{SO}_5 - \text{H}_2\text{O}$ ), or else the acid  $\text{H}_2\text{SO}_5$  is monobasic. The formation from potassium persulphate would then be expressed thus:



\* It is very doubtful whether hydrogen peroxide could be formed under these conditions, since it would have to be liberated in the presence of an excess of concentrated sulphuric acid. A further reaction would probably take place according to the equation  $\text{H}_2\text{O}_2 + 4\text{H}_2\text{SO}_4 = \text{H}_2\text{S}_4\text{O}_{14} + 4\text{H}_2\text{O}$ . There would then be a proportionately large decrease in the acidity, since six molecules of sulphuric acid disappear and only two molecules of Caro's acid are formed, assuming that  $\text{H}_2\text{S}_4\text{O}_{14}$  is dibasic. The results obtained indicate, in every case, an increase in acidity.

Here, again, for every molecule of Caro's acid formed the increase in acidity (expressed in grams  $\text{H}_2\text{SO}_4$ , and assuming that  $\text{H}_2\text{S}_2\text{O}_9$  is dibasic) is also equivalent to 1 molecule. In this case, however,  $\text{H}_2\text{S}_2\text{O}_9$  would liberate twice as much iodine as  $\text{H}_2\text{SO}_5$  from potassium iodide, and the ratio ( $\alpha$ ) should then become 5.18, whereas I formerly obtained the value 2.56.

The object of the present communication is to explain this discrepancy. In the experiments published the increase in acidity was measured by means of a solution of barium hydroxide which happened to be available at the time. When Caro's acid is neutralised with this alkali, it is at the same time decomposed (Baeyer and Villiger, *loc. cit.*), but this is of no consequence if the formula is  $\text{H}_2\text{SO}_5$  and the acid dibasic; if, however, the formula is  $\text{H}_2\text{S}_2\text{O}_9$  (or if  $\text{H}_2\text{SO}_5$  is monobasic), then the increase in acidity, as determined by the barium hydroxide, is twice what it should be, since 1 molecule of  $\text{H}_2\text{S}_2\text{O}_9$  will give, on decomposition, two molecules of sulphuric acid.

Sodium hydroxide, which only decomposes Caro's acid to a very small extent, should, on the other hand, give the theoretical value 5.18. The experiments were carried out according to the method given in the previous paper (*Ber.*, 1902, 35, 293). Caro's acid was made by the action of 5 c.c. of concentrated sulphuric acid on varying weights of potassium persulphate. Sulphuric acid was slowly added from a pipette to the finely powdered salt, the mixture being thoroughly stirred, and, after 50 minutes, diluted with ice, and then made up to 250 c.c.

Caro's acid was then estimated by the amount of iodine liberated from potassium iodide. This must be done in dilute solution, otherwise the unchanged persulphate and the excess of sulphuric acid present also liberate iodine. As is shown by the following figures obtained by Mr. A. D. Denning, B.Sc., who employed 5 c.c. of Caro's acid solution diluted with varying quantities of water, the reaction is complete in a very short time, concordant readings being obtained after 15 seconds, 1 minute, or 2 minutes when the dilution was 50 c.c. :

| Dilution. | Titration after 15 secs. | 1 min.     | 2 mins.    |
|-----------|--------------------------|------------|------------|
| 0 c.c.    | 28.99 c.c.               | 29.44 c.c. | 29.77 c.c. |
| 10 "      | 28.56 "                  | 28.79 "    | 29.18 "    |
| 20 "      | 28.49 "                  | 28.64 "    | 28.70 "    |
| 30 "      | 28.45 "                  | 28.51 "    | 28.52 "    |
| 40 "      | 28.45 "                  | 28.47 "    | 28.50 "    |
| 50 "      | 28.45 "                  | 28.49 "    | 28.48 "    |

It is especially necessary that the measurement of the 5 c.c. of the sulphuric acid should be exact, since the increase in acidity is very small

accordingly all pipettes, flasks, &c., used were carefully graduated. The results are trustworthy when the pipette takes about 5 minutes to deliver, as shown by the following numbers, each of which was obtained by adding 5 c.c. of concentrated sulphuric acid to water, diluting to 250 c.c., and titrating 2 c.c. of the solution against standard sodium hydroxide solution; the amounts of this reagent required were: 26.82, 26.88, 26.85, 26.84, 26.82 c.c. respectively. The titration of sulphuric acid with barium hydroxide gives accurate results, the error being less than 1 per cent.

Hydrogen peroxide was found to be present in small quantities in every case, unless special precautions were taken to keep the temperature as low as possible by means of freezing mixtures, the dilution being carried out in the presence of a large excess of ice. In order to estimate the peroxide, 25 c.c. of the solution were titrated with potassium permanganate, a little manganese sulphate having previously been added to act as a catalyser (Lowry and West, *loc. cit.*). That this method of estimation is not accurate, especially when Caro's acid is present in large excess, is shown by the following figures.

Varying quantities of a solution of Caro's acid containing only a small amount of hydrogen peroxide, as shown by titanium sulphate, were titrated, the same amount of manganese sulphate being added in each case. The titrations were:

|     |                    |                               |          |   |
|-----|--------------------|-------------------------------|----------|---|
| (1) | 5 c.c. Caro's acid | = 0.30 c.c. $\text{KMnO}_4$ . |          |   |
|     | 10 "               | "                             | = 0.42 " | " |
|     | 15 "               | "                             | = 0.60 " | " |
|     | 20 "               | "                             | = 0.69 " | " |
|     | 30 "               | "                             | = 0.94 " | " |
| (2) | 5 "                | "                             | = 1.75 " | " |
|     | 25 "               | "                             | = 6.15 " | " |

In another case, a mixture of hydrogen peroxide and Caro's acid was made and then titrated:

|                 |   |                             |
|-----------------|---|-----------------------------|
| 10 c.c. mixture | = | 5.60 c.c. $\text{KMnO}_4$ . |
| 25 " "          | = | 13.08 " "                   |

These discrepant titrations are not rendered concordant by diluting to the same volume, and the difference is not due to the want of sulphuric acid when the larger volumes are titrated.

Baeyer and Villiger suppose that manganese sulphate acts catalytically and decomposes Caro's acid, whereas, according to Bach (*Ber.*, 1900, 33, 3111), the hydrogen peroxide and Caro's acid are simultaneously decomposed by the permanganate, the action not being catalytic. If potassium permanganate solution is added to pure (diluted) Caro's acid (acid containing no hydrogen peroxide), there is



no action between the two, even after several hours (compare Baeyer and Villiger, *Ber.*, 1900, 33, 2488); on adding a little manganese sulphate, however, a slow reaction takes place, the permanganate being reduced and the acid decomposed. After a short time, a deposition of a higher oxide of manganese takes place and the evolution of gas becomes more marked, the supernatant liquid retaining a red colour, which is not due to permanganate. A similar reaction, due to the manganese sulphate formed, takes place when hydrogen peroxide is titrated in the presence of Caro's acid, but in this case it is possible that "chemical induction" also plays a part, as found by Schilow in similar cases (*Zeit. für Physikal. Chemie*, 1903, 42, 641).

Manganese sulphate alone also decomposes Caro's acid, and this would account for the excess of oxygen found by Bach in his titrations of a mixture of hydrogen peroxide and this acid.

Since the amount of hydrogen peroxide present was always very small, and in each case there was an *increase* in acidity (see footnote, p. 544), the accuracy of the measurement does not greatly matter, it being evident that the formula  $\text{H}_2\text{S}_4\text{O}_{14}$  will not hold for the diluted acid. The results obtained are given in Table I. The weights given represent the amounts in 250 c.c.

TABLE I.

| Weight of per-sulphate. | Hydrogen peroxide in grams. | Iodine equivalent in grams. | Increase in acidity in grams $\text{H}_2\text{SO}_4$ ( $\text{NaOH}$ ). | Ratio $a_1$ . | Increase in acidity in grams $\text{H}_2\text{SO}_4$ [ $\text{Ba}(\text{OH})_2$ ]. | Ratio $a_2$ . | Ratio $b$ . |
|-------------------------|-----------------------------|-----------------------------|---|---------------|--|---------------|-------------|
| 2                       | 0.00657                     | 1.613                       | 0.336   | 4.80          | 0.534  | 3.02          | 245.3       |
| 2                       | 0.00958                     | 1.613                       | 0.359   | 4.49          | 0.595  | 2.71          | 168.3       |
| 2                       | 0.01090                     | 1.588                       | 0.336   | 4.73          | 0.557  | 2.85          | 146.3       |
| 2                       | 0.00657                     | 1.493                       | 0.319   | 4.68          | 0.549  | 2.72          | 227.2       |
| 2                       | 0.00811                     | 1.632                       | 0.362   | 4.50          | 0.618  | 2.64          | 201.2       |
| 2                       | 0.00822                     | 1.594                       | 0.352   | 4.53          | 0.557  | 2.86          | 194.1       |
| 3                       | 0.00448                     | 2.395                       | 0.479   | 5.00          | 0.831  | 2.88          | 534.1       |
| 3.5                     | 0.00397                     | 2.720                       | 0.595   | 4.57          | 0.991  | 2.74          | 684.9       |
| 4                       | 0.00531                     | 3.191                       | 0.681   | 4.68          | 1.174  | 2.72          | 601.4       |
| Mean values .....       |                             |                             |   | 4.66          |  | 2.79          | 333.6       |

It is evident from the above table that the acid is not  $\text{H}_2\text{S}_4\text{O}_{14}$ , since the ratio "b" has a mean value of 333.6, and in every case an increase in acidity has taken place. The value of (a) varies with the alkali used in determining the increase in acidity, the mean values being 4.66 when sodium hydroxide\* is employed and 2.79 with

\* As a mean of more than twenty determinations, Mr. A. D. Denning has obtained the value 4.63.

barium hydroxide, the theoretical values being 5.18 and 2.59 respectively, if we assume that the acid is  $\text{H}_2\text{S}_2\text{O}_9$  (or  $\text{H}_2\text{SO}_5$  acting as a monobasic acid), and that it is decomposed by barium hydroxide when titrated, but not by sodium hydroxide. The discrepancy existing between the observed and calculated ratios can be accounted for if we assume:

(1) That a slight decomposition of Caro's acid takes place when it is titrated with sodium hydroxide.

(2) That the decomposition is not quite complete when barium hydroxide is used to neutralise the acid.

A fresh series of experiments was made with a view to testing these hypotheses, the results being given in the following table:

TABLE II.

| Weight of persulphate. | Iodine equivalent in grams. | Increase in acidity in grams $\text{H}_2\text{SO}_4$ ( $\text{NaOH}$ ). | Ratio $a_1$ . | Increase in acidity in grams $\text{H}_2\text{SO}_4$ [ $\text{Ba}(\text{OH})_2$ ]. | Ratio $a_2$ . | Corr. ratio $a_2$ . |
|------------------------|-----------------------------|---|---------------|--|---------------|---------------------|
| 3                      | 2.209                       | 0.445   | 4.97          | 0.746  | 2.96          | 2.67                |
| 3                      | 2.205                       | 0.440   | 5.01          | 0.725  | 3.04          | —                   |
| 3                      | 2.227                       | 0.483   | 4.61          | 0.739  | 3.01          | 2.67                |
| 3*                     | 2.373                       | 0.517   | 4.59          | 0.806  | 2.94          | 2.62                |
| 3                      | 2.332                       | 0.469   | 4.97          | 0.752  | 3.10          | 2.73                |
| 3                      | 2.243                       | 0.450   | 4.99          | 0.699  | 3.21          | 2.83                |
| 5                      | 3.399                       | 0.715   | 4.75          | 1.021  | 3.39          | 2.81                |
| 5 (?)                  | 3.617                       | 0.789   | 4.59          | 1.117  | 3.24          | 2.69                |
| Mean values .....      |                             |   | 4.81          |  | 3.11          | 2.71                |

Somewhat larger quantities of potassium persulphate were taken, so as to decrease the error of measurement, although much greater amounts could not be employed, since the potassium sulphate formed is so sparingly soluble in cold water.

*Ratio  $a_1$ .*—The value obtained is slightly greater than that given in Table I, but it is still somewhat lower than the theoretical. No decomposition takes place on titration, as is shown by the following results. Two c.c. of Caro's acid were diluted to 50 c.c., potassium iodide added, and the liberated iodine titrated with sodium thiosulphate. The titrations in three determinations were 15.21, 15.25, and 15.25 c.c. Two c.c. were then neutralised with sodium hydroxide, afterwards acidified, the volume made up to 50 c.c., potassium iodide added, and the liberated iodine determined; the titrations were 15.18 and 15.20 c.c., or practically the same values as before neutralising.

It is possible that Caro's acid is decomposed on neutralising with the

formation of hydrogen peroxide, and thus the same amount of iodine is set free before and after neutralisation with sodium hydroxide, since 1 molecule of hydrogen peroxide liberates the same amount of iodine as 1 molecule of Caro's acid ( $\text{H}_2\text{SO}_5$ ).<sup>\*</sup> If, however, *pure* Caro's acid is neutralised with sodium hydroxide, under the same conditions as above, then hydrogen peroxide is not formed, as shown by the test with titanium sulphate. Since no decomposition takes place on titrating, the low value of "*a*" cannot be explained on this assumption. It is possibly due to experimental errors, since the values observed vary from 4.59 to 5.01, this variation being greater than that of the theoretical amount from the mean value of the experimental numbers.

*Ratio  $a_2$ .*—The mean value in Table II is 3.11, which is greater than that in Table I, but in both cases the values are greater than the theoretical.

By applying the tests employed in the case of sodium hydroxide, it was found that (1) the decomposition due to neutralisation was not quite complete, and (2) that hydrogen peroxide was not formed during the decomposition under the conditions of experiment.<sup>†</sup>

The amount of decomposition depends on the strength of the solutions used and on the time of titration, so that concordant results cannot be obtained. This explains the higher value 3.11 indicated in Table II. The amount of decomposition is shown by the following results. Two c.c. of Caro's acid before neutralisation had an iodine equivalent of 16.24 c.c. of thiosulphate. After neutralisation with barium hydroxide, the iodine equivalent was only 3.60 c.c. of thiosulphate.

These numbers serve to give an idea of the amount of decomposition, and, knowing this, the corrected value of  $a_2$  can be calculated by supposing that the amount of Caro's acid present would give an increase in the acidity of  $x$  c.c. of barium hydroxide, if no decomposition took place, whereas the increase would be  $2x$  c.c. of barium hydroxide if the decomposition were complete. Let the decomposition be  $a$ , then the undecomposed Caro's acid is  $1 - a$ ,

$$\text{and } \therefore \text{ increase in acidity} = (1 - a)x + 2ax \text{ c.c. Ba(OH)}_2 \\ = (x + ax) \text{ c.c.}$$

<sup>\*</sup> Hydrogen peroxide liberates iodine comparatively slowly from potassium iodide, so that a titration made within one minute would not indicate the whole of this compound. Since the results obtained before and after neutralisation were concordant, it would appear that hydrogen peroxide is absent. The amount of sulphuric acid present must not be too great, however, otherwise iodine is liberated by its action on potassium iodide.

<sup>†</sup> If a concentrated solution of barium hydroxide is added to a strong solution of Caro's acid, small quantities of hydrogen peroxide seem to be formed, as indicated by the titanium sulphate test.



In the above case (marked \* in Table II),

$$\alpha = \frac{16.24 - 3.60}{16.24} = 0.78,$$

$$\therefore x + 0.78x = \text{increase in number of c.c. Ba(OH)}_2 \\ = 0.8060 \text{ gram H}_2\text{SO}_4 \text{ per 250 c.c.}$$

$$\therefore 2x = 0.9056 \quad \text{,,} \quad \text{H}_2\text{SO}_4 \quad \text{,,}$$

and  $\therefore$  corrected ratio  $(a_2) = \frac{2.373}{0.9056} = 2.62$ , which agrees with the theoretical value. The mean of the corrected values is 2.71, which is slightly greater than the theoretical value, the difference being probably due to experimental error.

The results thus obtained are in agreement with those of Armstrong and Lowry, the formula for Caro's acid being either  $\text{H}_2\text{SO}_5$  (monobasic) or  $\text{H}_2\text{S}_2\text{O}_9$  (dibasic).

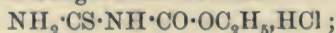
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# LXI.—*Salts of a Mercaptoid Isomeric Form of Thioallophanic Acid, and a New Synthesis of Imino-carbaminethioalkyls.*

By AUGUSTUS E. DIXON, M.D.

IN a communication published from the author's laboratory in 1896 (Trans., 69, 324), it was shown by R. E. Doran that from ethyl chlorocarbonate and lead thiocyanate, a carbethoxythiocarbimide can be obtained, which unites with ammonia, thereby yielding carbethoxythiourea,  $\text{EtO} \cdot \text{CO} \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{NH}_2$  (or, assuming it to be of the thiocarbamidic type,  $\text{EtO} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$ ), melting at 139—140°.

It is uncertain whether this carbethoxythiourea is identical or not with a product obtained by Peitzsch (Ber., 1874, 7, 896) from ethoxalyl chloride and thiourea, for the latter is mentioned only in a preliminary notice, and the description is limited to the statement that it occurs in colourless, rhombic prisms, having the formula  $\text{C}_4\text{H}_5\text{O}_2\text{N}_2\text{S}$ . Later on, Pawlewski (Ber., 1888, 21, 402) obtained from ethyl chlorocarbonate and thiourea a solid, to which, from the result of two chlorine determinations, he assigned the formula



it melted at 117°, and was regarded by him as being probably the hydrochloride of Peitzsch's compound.

There are difficulties in the way of accepting this constitution, for, apart from its isomerism with Doran's compound, substituted thioureas

containing electro-positive groups either do not form hydrochlorides, or else yield them with difficulty, and hence, if substitution were to occur at a nitrogen atom by means of the electro-negative carbethoxy-group, it seems reasonable to anticipate that the power to form a hydrochloride would now be lost.

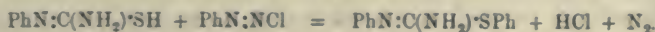
But supposing Pawlewski's compound to be a hydrochloride, and, consequently, the atomic complex,  $C_4H_6O_2N_2S$ , to have basic properties, it seemed not unlikely that this supposed  $NH_2 \cdot CS \cdot NH \cdot CO_2Et$ , might be constituted similarly to the basic derivatives obtained from thio-ureas by combination with alkylogens, these being represented by the generic formula  $NH_2 \cdot C(NH) \cdot SR$ , where R stands for any hydrocarbon group not purely benzenoid in character.\*

Several years ago, the author having occasion to test this conjecture experimentally, the substance was re-examined in sufficient detail to distinctly establish its general character, and from the results, which were described in a "Note on ethyl isothioallophanate," incorporated in Mr. Doran's paper (*loc. cit.*, 339), the compound was inferred to be the hydrochloride of a base,  $NH:C(NH_2) \cdot S \cdot CO_2Et$ , that is, carbethoxy- $\psi$ -thiourea.

According to M. Seidel (*J. pr. Chem.*, 1885, 32, 261—277), phenylthiourea and ethyl chlorocarbonate interacted with evolution of hydrogen chloride, carbon dioxide, and ethyl chloride, giving a yellow oil, from which yellow crystals slowly separated; these could not be freed from the adherent oil by washing, because on contact with solvents the mixture was decomposed. Nevertheless, the oily product was analysed, with results leading to the formula  $C_{10}H_{12}O_2N_2S$ ; the presence of sulphur was ascertained by qualitative tests, but its amount was not determined. All attempts to ascertain which hydrogen atom of the phenylthiourea was replaced by  $CO_2Et$  proved fruitless. But as Miquel had already established the symmetry of acetylphenylthiocarbamide, and of the corresponding benzoylethyl derivative, the author decided to represent his "Carboxyaethylphenyl-sulfoharnstoff" by the constitutional formula  $CS < \begin{smallmatrix} NH \cdot C_6H_5 \\ NH \cdot CO \cdot OC_2H_5 \end{smallmatrix}$ , notwithstanding that a compound such as  $NH:C(NHPh) \cdot S \cdot CO_2Et$  might have been expected to result from the above interaction.

It may be noted that the conclusion drawn by Seidel regarding the position assumed by a negative substituting group is hardly justifiable;

\* There is, of course, no reason why a purely aromatic group should not enter into such combination, but the aryl haloids appear incapable of direct interaction. The author has made several unsuccessful attempts to effect union, by treating phenylthiourea, or its sodium derivative, with the solution of a diazobenzene salt, in the hope of realising, for example, the change:



in Miquel's syntheses (from acetyl and benzoyl thiocarbimides), the negative radicle was already combined with a nitrogen atom, but it does not follow that when introduced by means of its haloid derivative, the radicle must necessarily become so attached.

However, whilst Doran's investigations (*loc. cit.*) render it quite certain that the product obtained by Seidel from ethyl chlorocarbonate and phenylthiourea was not *ab*-carbethoxyphenylthiocarbamide, it remained to repeat Seidel's experiments in order to ascertain the composition of the unstable yellow oil; this has now been done, and the investigation extended so as to include other varieties of thioureas, but with results so different from those of Seidel, that the author, being unable either to reconcile them, or to account satisfactorily for the discrepancies, must rest content with a description of his own experiments.

Preliminary trials showed the results to be dependent on the temperature; for if heat were applied, gas was freely evolved, whilst little or none escaped from mixtures allowed to remain in the cold, although interaction also took place in the latter circumstances. However, as Seidel, working at the temperature of the water-bath, had observed the evolution of gases, a first series of experiments was conducted under like conditions, the general results thus obtained being incorporated in Part I of the present paper.

#### Part I.—*Experiments Conducted under the Influence of Heat.*

##### *Action of Ethyl Chlorocarbonate on Phenylthiourea.*

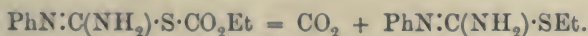
On warming on the water-bath the mixture containing excess of chlorocarbonate, diluted with two or three times its own volume of dry benzene, in a flask provided with reflux condenser, interaction set in before the boiling point was reached, the powdered solid melting to a viscid oil, which quickly swelled up into a vesicular paste. The escaping gas consisted mainly of carbon dioxide; it did not affect lead acetate paper, but traces of ethyl chlorocarbonate were carried over in the stream of carbon dioxide. In an hour or so, the effervescence had ceased, and the product now formed two layers, the under one consisting of the oil, and the upper of benzene, in which, at ordinary temperatures, the oil is nearly insoluble; when cold, the oily layer became so viscid that the flask could be inverted and the benzene drained off, the residue being then washed, first with more benzene, and then with light petroleum.

Provided that a good excess of chlorocarbonate had been used, and the heating sufficiently prolonged, the residual oil was almost completely soluble in cold water (otherwise unchanged phenylthiourea



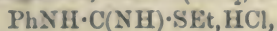
separated), yielding a feebly acid solution, which proved to contain a hydrochloride, and when mixed with aqueous caustic alkali, had an odour of mercaptan, this becoming very pronounced and disagreeable on warming. By cautious treatment with caustic alkali, or alkali carbonate, a clear, almost colourless oil was precipitated, and extracted with ether; this product, which was highly basic and free from chlorine, gave, in warm alcoholic solution, a dirty yellow precipitate with ammoniacal silver nitrate; or a bright yellow precipitate if dissolved in excess of caustic potash and treated with a lead salt. From these properties, it was clear that union had occurred through the sulphur of the phenylthiourea, though presumably not with formation of  $\text{PhN:C}(\text{NH}_2)\cdot\text{S}\cdot\text{CO}_2\text{Et}$ , since the latter would yield  $\text{EtO}\cdot\text{CO}\cdot\text{SH}$  on hydrolysis, and thence hydrogen sulphide; whilst the yellow precipitates showed the presence of metallic mercaptide.

But since mercaptide is formed, the ethyl group must have entered into direct combination with the sulphur atom; an unexpected result, but one easily explained, by supposing the phenylthiourea to unite with the chlorocarbonate, so as to form an additive product,  $\text{PhN:C}(\text{NH}_2)\cdot\text{S}\cdot\text{CO}_2\text{Et}, \text{HCl}$ , the basic residue of which then decomposes according to the equation:



In order to learn whether the carbon dioxide was evolved in an amount consistent with such a view, molecular proportions of the constituents, mixed with a little dry toluene, were very gently warmed until all sign of effervescence had ceased. During the operation, air freed from moisture and carbon dioxide was slowly drawn through the apparatus, the products being passed, first into a strong solution of silver nitrate, and eventually into a weighed potash-bulb. The silver solution only became slightly opalescent, and consequently the evolution of hydrogen chloride was negligible, but a little hydrogen sulphide came over, for darkening of the solution occurred; the weight of carbon dioxide absorbed in the potash-bulb was equal to fifteen-sixteenths of that theoretically producible from the quantity of chlorocarbonate taken for experiment.

Large, well-formed rhomboidal crystals gradually separated from the oily reaction-product; these were soluble in water, and probably consisted of the hydrochloride,  $\text{PhN:C}(\text{NH}_2)\cdot\text{SEt}, \text{HCl}$  or



but could not be freed from the accompanying viscid oil.

In view of the mode of formation of this hydrochloride, and the readiness with which the corresponding base decomposed, even at the ordinary temperature, yielding mercaptan, there could be little doubt as to its identity with Bertram's ethyl ester of iminophenylthio

carbamic acid (iminophenylcarbaminethioethyl), obtained from ethyl iodide and phenylthiourea (*Ber.*, 1892, 25, 55); this is described as a colourless liquid, easily decomposed by caustic alkalis, with production of mercaptan, and forming a picrate melting at 196°. For the purpose of further identification, this salt was prepared; when twice recrystallised from boiling water, it formed bright yellow prisms melting at 196—197° (corr.), and giving, with warm silver nitrate and ammonia, a clear yellow precipitate.

*Action of Methyl Chlorocarbonate on Phenylthiourea.*—A moderate excess (about  $1\frac{1}{2}$  mols.) of chlorocarbonate was used in the presence of benzene; if the solvent is omitted, the product is a stiff glue, distended by the escaping gas into a bulky froth, which tends to rise out of the liquid; chlorocarbonate gradually volatilises, even although a reflux condenser is used, and it is desirable, when the action seems to be complete, to add a little more of this reagent, and heat for another half-hour.

As in the preceding case, hydrochloric acid was not liberated in notable quantity, neither could hydrogen sulphide be detected, although carbon dioxide came off abundantly; the residue, when freed from benzene by washing with light petroleum, formed a viscid pale syrup, dissolving readily in cold water if the action had been completed; its chemical properties resembled those of the product obtained from ethyl chlorocarbonate.

By treating the dilute aqueous solution with normal caustic alkali until precipitation just ceased, the corresponding base was liberated; oily at first, but quickly hardening to a white, apparently crystalline, solid; this, when recrystallised, first from weak spirit, and then from boiling light petroleum, separated in long, slender, brilliant prisms melting at 69—70° without decomposition. When cold, the base was practically odourless, but smelt very foully if heated much above 100°. It was soluble in excess of caustic alkali, the solution giving, with lead acetate, a clear, bright yellow precipitate, which dissolved on further heating, the liquid remaining colourless and clear, even when boiled; moreover, the alcoholic solution, if treated with neutral or ammoniacal silver nitrate, showed not the least sign of desulphurisation, but gave instead a bright yellow precipitate. The base was strongly alkaline, free from chlorine, and decomposed very readily when warmed with solution of caustic potash, evolving mercaptan:

Found N = 16.9, 17.0, 17.1; S = 18.8.

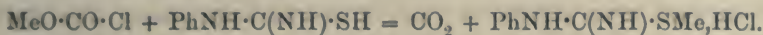
$C_8H_{10}N_2S$  requires N = 16.9; S = 19.29 per cent.

In order to confirm the identity of this substance with Bertram's methyl ester of iminophenylthiocarbamic acid or iminophenylcarbaminethiomethyl (*loc. cit.*, 49), the acetate, picrate, and hydriodide



were also prepared and examined. The first of these salts melted at  $114-115^{\circ}$ ; the second formed large, rectangular scales, melting at  $176-177^{\circ}$ , and having a splendid lustre, resembling that of burnished brass; the third was obtained in almost white needles, melting at  $145-146^{\circ}$ , and giving 9.5 per cent. of nitrogen, against 9.55 calculated for  $C_8H_{10}N_2S \cdot HI$ . Bertram's figures are  $115^{\circ}$ ,  $175^{\circ}$ , and  $147^{\circ}$  respectively; for the melting point of the pure base, he gives  $71^{\circ}$ , whilst that observed in the present instance was  $69-70^{\circ}$ .

Methyl chlorocarbonate, therefore, when heated with phenylthiourea, behaves similarly to its ethyl homologue, the interaction occurring substantially as follows:



The yield of crude hydrochloride was generally almost quantitative; and the weight of precipitated base often reached 84 per cent. of the theoretical.

#### *Action of Methyl Chlorocarbonate on p-Tolylthiourea.*

The product formed a clear syrup, almost entirely soluble in cold water, and evolving mercaptan when warmed with caustic alkali; by allowing the solution in alcohol to evaporate slowly, it was obtained in moist, dirty yellow prisms, the yield of crude material being approximately quantitative.

The salt was dissolved in a little absolute alcohol, and treated with ether, whereby an oil was precipitated, soon changing to a crystalline solid; the latter, however, was still impure, for its aqueous solution (which was neutral to litmus) became brown on treatment with ammonia and silver nitrate; moreover, the melting point was very indistinct. The solid effervesced with sulphuric acid, giving off fumes of hydrogen chloride, and its cold, aqueous solution yielded a white precipitate of silver chloride on the addition of neutral silver nitrate.

To obtain the corresponding base, a quantity of the hydrochloride was mixed with cold water, and a small residue collected; when purified by recrystallisation from alcohol, this melted at  $182-183^{\circ}$ , and was identified as *p*-tolylthiourea. On treating the clear filtrate with normal alkali, a clear, basic oil was precipitated, having chemical properties similar to those of its congeners. A nitrogen determination, made with the crude oil, showed  $N = 15.3$  per cent.; this figure is rather low for  $C_9H_{12}N_2S$ , which would require  $N = 15.59$  per cent. The base was now dissolved in weak hydrochloric acid; from the solution, when reduced to a small bulk, long, white prisms were deposited, rather deliquescent, and melting at  $154-155^{\circ}$ . A determination of the combined hydrochloric acid, by Volhard's method, gave  $HCl = 16.2$ ,



and nitrogen was found to be 13.0 and 13.1 per cent. ;  $C_9H_{12}N_2S.HCl$  would require,  $HCl = 16.83$ , and  $N = 12.96$  per cent. With alkaline lead or silver salts, the solution now gave clear, bright yellow precipitates, yielding practically no trace of metallic sulphide, even when boiled. From the salt thus purified, the base, *imino-p-tolylcarbamethiomethyl* [*methyl imino-p-tolylthiocarbamate*], was displaced once more by alkali, but still formed an oil, which showed no tendency to become solid.

*Action of Methyl Chlorocarbonate on o-Tolylthiourea.*

The process was carried out as previously described ; the product, a clear, yellow oil, after a while became very viscid, its chemical characters being similar to those of the para-compound. The yield was almost quantitative, but the oil showed marked desulphurisation with ammonia and silver nitrate, and the combined hydrochloric acid was found to be 0.8 per cent. below the figure calculated for  $C_9H_{12}N_2S.HCl$ . When mixed with water, some unchanged *o*-tolylthiourea separated (3 per cent. of the amount employed), and the filtered solution, which was not quite clear, had a distinct odour of thiocarbimide. By treatment with normal caustic alkali, the free base was obtained ; it formed a granular powder, melting at  $100-101^\circ$ , and was very nearly pure ; for although a trace of silver sulphide was visible on treating the alcoholic solution with silver nitrate, the percentage of nitrogen proved to be 15.6, instead of 15.59, calculated for  $C_9H_{12}N_2S$  ; the yield was 81 per cent. of the theoretical. When recrystallised from boiling light petroleum, and then from dilute alcohol, it separated in white, lozenge-shaped prisms, melting at  $101-102^\circ$ , very freely soluble in alcohol, nearly insoluble in water, and highly alkaline to litmus, &c. Silver nitrate no longer caused any desulphurisation, and the nitrogen was now found to be 15.7 per cent.

In all its general chemical properties this compound, *imino-o-tolylcarbamethiomethyl* [*methyl imino-o-tolylthiocarbamate*] precisely resembles its congeners, described above.

*Action of Methyl Chlorocarbonate on Allylthiourea.*

The hydrochloride formed a syrup, subsequently changing to a deliquescent solid, the melting point of which could not be determined satisfactorily ; it was insoluble in carbon disulphide or light petroleum, nearly so in benzene, but easily soluble in water, alcohol, or chloroform ; from the latter it was precipitated by ether as an oil, which in a little time deposited vitreous prisms, these being further purified by precipitating the alcoholic solution by ether :

$HCl = 21.7$ .  $N = 16.9$  and  $16.9$ .

$C_3H_6N_2S.HCl$  requires  $HCl = 21.88$ , and  $N = 16.86$  per cent.

With alkaline lead and silver salts, clear, bright yellow precipitates were obtained; caustic alkali, when added to the aqueous solution (which is neutral—this property being common to the hydrochlorides of all such bases when they are pure) gave no precipitate, but the mixture decomposed very readily, even without application of heat, yielding mercaptan.

As the deliquescent hydrochloride proved rather difficult to handle, and there seemed to be little prospect of isolating the corresponding unstable base in a pure condition, its picrate was prepared; this salt formed brilliant, orange-yellow, flexible, hair-like needles containing no chlorine and melting at  $149-150^{\circ}$  (corr.). Warm caustic alkali dissolves this substance freely, the solution having a disagreeable odour of mercaptan, and the escaping vapour turning lead acetate paper yellow. A nitrogen determination gave  $N = 19.5$ .  $C_5H_{10}N_2S, C_6H_3O_7N_3$  requires  $N = 19.54$  per cent.

#### *Methyl Chlorocarbonate and Carbethoxythiourea.*

Interaction readily occurred on warming; after the benzene had been expelled, cold water extracted from the residue a white, somewhat deliquescent, crystalline solid. When warmed with caustic alkali, the product smelt of mercaptan, and gave with lead acetate solution a yellow precipitate, and hence, no doubt, consisted in part of the hydrochloride of *iminocarbethoxycarbaminethioethyl* [*ethyl iminocarbethoxythiocarbamate*],  $EtO \cdot CO \cdot NH \cdot C(NH) \cdot S \cdot Et$ , but the solution was markedly desulphurised by ammonia and silver nitrate; the quantity of material obtained amounting to only a few grams, and the proportion of impurity being apparently considerable, the product was not further examined.

So far as may be judged from the foregoing experiments, the interaction between alkyl chlorocarbonates and monosubstituted thioureas would appear to be generic; it remained to be seen whether symmetrical disubstituted thiocarbamides would yield compounds of a similar class, for instance,  $PhNH \cdot C(NPh) \cdot S \cdot Et$ . According to Seidel (*loc. cit.*), this is not the case, for ethyl chlorocarbonate and thiocarbamilide condense with elimination of hydrochloric acid, to yield the trisubstituted thiocarbamide,  $PhN(CO_2Et) \cdot CS \cdot NHPh$ , which melts at  $95^{\circ}$ . In order to verify this statement, the interaction was re-examined.

#### *Action of Ethyl Chlorocarbonate on Diphenylthiocarbamide.*

The constituents named were gently heated as before, and yellow needles obtained, which, when purified by recrystallisation, became colourless and melted sharply at the temperature given by Seidel, namely,  $95^{\circ}$ .



The product was somewhat acid to litmus, and free from chlorine; a nitrogen determination gave 9.5 per cent., whilst  $C_{16}H_{16}O_2N_2S$  would require  $N = 9.35$ . It was insoluble in water, but dissolved in warm, dilute caustic alkali, evolving no odour of mercaptan; when lead acetate was added to the alkaline solution, no yellow precipitate appeared, but on heating the mixture, a dense, black sediment was produced, consisting of lead sulphide. Since this compound does not retain the hydrochloric acid formed, it cannot be an analogue of those previously described; moreover, from the fact that, on hydrolysis, hydrogen sulphide is produced, but no mercaptan, it follows that the sulphur is not combined with the ethyl group.

In this case, Seidel was probably correct in assuming the carbethoxy-group to be attached to nitrogen, for the product exhibits no distinctly basic character. Nevertheless, the absence of this character is by itself insufficient to definitely establish the position of the carbethoxy-group; but as the present study is meant to include nothing beyond the chemistry of monosubstitution derivatives, the question may be left for a future paper.

An experiment similar to the foregoing was conducted, using methyl chlorocarbonate; the product, a homologue of Seidel's compound, separated in white needles, melting at  $105^\circ$ , having similar properties to the ethyl derivative, and giving 9.6 of nitrogen, against 9.8 per cent., calculated for  $C_{15}H_{14}O_2N_2S$ .

Briefly stated, the results now substantiated are the following:

Monosubstituted thioureas interact readily with chlorocarbonates; carbon dioxide is expelled, and a "pseudothiurea" hydrochloride formed, the sulphur of which is attached to the hydrocarbon residue of the chlorocarbonate; diphenylthiocarbamide, on the other hand, takes up the whole carboxyalkyl group, with loss of hydrochloric acid.

## Part II.—*Experiments Conducted in the Cold.*

In conducting the experiments described below, no external heat was applied.

### *Methyl Chlorocarbonate and Phenylthiourea.*

Finely sifted phenylthiourea, suspended in dry benzene, was treated with a considerable excess of methyl chlorocarbonate, the containing vessel being provided with a calcium chloride tube, in order to prevent the access of atmospheric moisture; the mixture did not become appreciably warm, nor was there any perceptible evolution of gas. After an hour, the solid product, which contained much chlorine, and had become almost entirely soluble in cold water, was now triturated



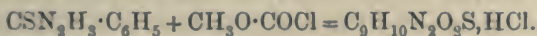
in a mortar, returned to the containing vessel along with the liquid, and kept for about thirty hours, at the end of which time it dissolved easily in water, and the action was therefore judged to be complete. The filtered product was washed with benzene, then with light petroleum, and exposed to warm air for several hours; when dry, its weight amounted to 98 per cent. of that theoretically producible, on the assumption that union had occurred in molecular proportion. The aqueous solution was strongly acid, gave the usual reactions of a hydrochloride, and melted at 86—87°, with copious effervescence.

Partial analysis led to the following results :

Found N = 11.40 ; S = 12.5. 10.4 grams, dissolved in water, required for neutralisation 42 c.c. *N*-alkali ; or HCl = 14.7.

$C_9H_{10}N_2O_3S$ , HCl requires N = 11.39, S = 13.00, HCl = 14.78 per cent.

Direct union therefore occurs in the cold between the constituents, with formation of a hydrochloride :



To learn whether this substance would readily lose carbon dioxide, so as to afford Bertram's ethyl iminophenylthiocarbamate,  $PhNH \cdot C(NH) \cdot SMe$ , a portion was dissolved in cold water and the solution heated. Before the boiling point was reached, a solid began to separate, some gas was evolved, and later on a trace of phenylthiocarbimide. After boiling gently for half an hour, the process was stopped; the residual liquid now contained hydrochloric acid, but gave no reaction for aniline. When recrystallised a few times from alcohol, the solid product was obtained in short, brilliant, vitreous prisms, free from chlorine, and melting with effervescence, at 167° (corr.). Obviously, therefore, Bertram's compound (m. p. 71°) was not present; moreover, the analysis gave N = 13.4, and S = 15.4; whilst the substance referred to would require N = 16.9, and S = 19.29 per cent. A description of the properties of this product may be omitted, as it was found to be identical with the next.

*Action of Caustic Alkali on the Hydrochloride.*—A weighed quantity was dissolved in plenty of cold water, and normal alkali allowed to flow in slowly; a precipitate appeared at once, quickly redissolving at first, but soon becoming permanent; it consisted of oily globules, which quickly solidified, and the point at which no further precipitation could be observed to occur coincided almost exactly with that of the neutrality of the solution. Using 5.2 grams, neutrality was attained when 21.2 c.c. had been used, corresponding with 14.95 per cent. of HCl absorbed; this figure, obtained from a different preparation, agrees approximately with that mentioned under the partial analysis of the hydrochloride. The semi-crystalline precipitate thus obtained

was collected, and washed thoroughly with water, in which it is practically insoluble; the filtrate had a faint odour of phenylthiocarbimide, and when acidified, gave no sign of effervescence, thus showing that alkali carbonate had not been produced; on evaporation to dryness, it left a white mass containing little else beside alkali chloride.

When recrystallised a few times from boiling alcohol, in which it is moderately soluble, the main product formed brilliant prisms, free from chlorine, nearly insoluble in light petroleum, indistinguishable in appearance from those obtained by heating the aqueous solution of the hydrochloride, and melting, with copious effervescence and evolution of gases smelling of mercaptan, at the same temperature as the by-product, namely,  $166-167^{\circ}$  (corr.). A mixture of the two in approximately equal proportion showed no change of melting point, and their identity was further confirmed by the results of analysis, which led to the formula  $C_9H_{10}O_2N_2S$ :

Found C = 50.65, 50.9; H = 4.7, 5.1; N = 13.4; S = 15.5, 15.4.

Calculated C = 51.43; H = 4.76; N = 13.33; S = 15.24 per cent.

In addition to those already mentioned, the following properties were observed: (1) When boiled with dilute caustic potash, little or no alkaline vapour was evolved, and there was no odour of mercaptan or other sulphuretted gases; the residual liquor, after cooling, gave the reactions of aniline, and when acidified, evolved hydrogen sulphide, together with carbon dioxide, and on treatment with ferric chloride, assumed a very deep red colour, thereby showing the presence of thiocyanic acid in considerable quantity. (2) When boiled with alkaline lead tartrate, desulphurisation soon commenced, but did not proceed to any notable extent; it was suspected, in fact, that this action might be due to the presence of a trace of some desulphurisable impurity, but the phenomenon still persisted after many recrystallisations, and was shown equally by the product obtained from the hydrochloride by heating its aqueous solution, and by that precipitated from it by alkali; most of the sulphur, therefore, is hydrolysed into thiocyanic acid under this treatment. (3) The cold alcoholic solution gave no precipitate with a few drops of silver nitrate, but the mixture at once began to change colour, slowly becoming red, then deep crimson, and finally black; with the ammoniacal nitrate, a thick precipitate of silver sulphide was at once produced.

On comparing the properties of the hydrochloride with those of the derivative,  $C_9H_{10}O_2N_2S$ , it is evident that the basic character of the latter is very feebly marked; for in its combination with this residue, the added hydrogen chloride displays just the same acidity as if it were free, and is completely separated by warming the aqueous solution. The mere act of dissolution is not alone sufficient to permanently



remove the acid, for when its solution in nearly anhydrous alcohol (which is strongly acid to litmus) is mixed with ether, the hydrochloride separates unchanged.

*Constitution of the Compound,  $C_9H_{10}O_2N_2S$ .*—Since thiocyanic acid is so readily formed by hydrolysis, it may be inferred that one of the nitrogen atoms must either be hydrogenised only, or else combined with a group which is easily withdrawn; such a group cannot possess a distinctly positive character.

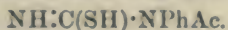
Differing as it does from the parent phenylthiourea, by  $MeO \cdot CO$  in the place of one hydrogen atom, the presumption is that this group exists as such in the molecule. If this be so, there is a tolerably liberal choice in the matter of formulæ:

- I,  $PhNH \cdot CS \cdot NH \cdot CO_2Me$ ; II,  $PhN(CO_2Me) \cdot CS \cdot NH_2$ ;  
 III,  $PhNH \cdot C(SH) : N \cdot CO_2Me$ ; IV,  $PhN : C(SH) \cdot NH \cdot CO_2Me$ ;  
 V,  $PhN(CO_2Me) \cdot C(SH) \cdot NH$ ; VI,  $PhNH \cdot C(NH) \cdot S \cdot CO_2Me$ ;  
 VII,  $PhN : C(NH_2) \cdot S \cdot CO_2Me$ .

Of these, No. I may be excluded; it represents *ab*-carbomethoxy-phenylthiocarbamide, a substance which has already been obtained by Doran (*Trans.*, 1901, 79, 908), and shown to melt at  $158^\circ$ , without decomposition.

Nos. III, IV, and Nos. VI, VII, are respectively tautomeric. Counting these pairs, therefore, as identical for practical purposes, the choice lies between II, III, V, and VI.

Much difficulty was at first experienced in attempting to decide between these constitutions, hydrolytic methods being obviously unavailable when dealing with a group such as  $CO_2Me$ , which is readily expelled, and must afford methyl alcohol and carbon dioxide in exchange for a hydrogen atom. However, the fact that thiocyanic acid was formed by the action of alkali, seemed to favour II, or its labile form V; for Hugershoff has shown (*Ber.*, 1899, 32, 3659) that isomeric acetylphenylthiocarbamide yields this acid when treated with strong alkali, its congeners behaving in like manner; and Wheeler, in turn, has shown (*Amer. Chem. J.*, 1902, 27, 270) that in this substance both the acetyl and the hydrocarbon radicle are combined with the same nitrogen atom, either as  $PhNAc \cdot CS \cdot NH_2$ , or



Against this view, there stands the fact that when the chlorocarbonate is warmed with the thiourea, a  $\psi$ -derivative results, as shown in the first series of experiments here recorded; and, since the former is not decomposed when heated alone, the source of the liberated carbon dioxide is not easy to understand, unless an additive compound is first produced, and if such is formed by union with nitrogen, there seems to be no intelligible reason why, on its decomposition, the methyl



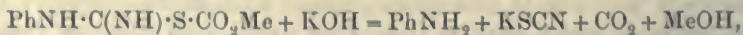
group should migrate and become attached to the sulphur atom, which is already satisfied.

No information was to be expected from the decomposition of the compound by heat, since at the high temperature of fusion, complete disruption of the molecule took place. It was remarked, however, that the hydrochloride, when fused, gave off no sulphuretted gases, and since it melted at a temperature far below that at which the corresponding "base" is decomposed, it had been taken for granted that the fusion entailed merely the loss of the feebly held hydrochloric acid. A duplicate determination of this melting point ( $87^\circ$ ), led to the observation that the fused product did not resolidify, as might have been expected, if, by loss of hydrogen chloride, the residue  $C_9H_{10}O_2N_2S$ , melting at  $167^\circ$  had been produced; moreover, the escaping gas was practically odourless, and therefore probably carbon dioxide. But if this gas alone was evolved, it was easy to ascertain whence it came; for if from attachment with nitrogen, the product must be unsymmetrical (or possibly symmetrical) phenylmethylthiourea, whereas if from the sulphur, Bertram's  $\psi$ -compound,  $PhN:C(NH_2) \cdot SCH_3$ , must result.

To elucidate this point, a quantity of the dry hydrochloride was heated on the water-bath; it slowly melted, with effervescence, and the resulting gas was shown to consist of carbon dioxide only; after prolonged heating, a trace of hydrogen chloride began to appear, and the process was then stopped. The residue formed a clear oil, which thickened into a resin on cooling; when mixed with water, all dissolved, except a trace of phenylthiourea, and the solution, when warmed with caustic alkali, smelt foully of mercaptan, and the cooled liquor gave a thick, bright yellow precipitate with lead acetate. Treatment with ammonia and silver nitrate gave marked desulphurisation, doubtless on account of the presence of phenylthiourea, but on filtering and warming the filtrate, a clear yellow precipitate was formed in abundance. These results are inconsistent with the formation of unsymmetrical phenylmethylthiourea,  $MePhN \cdot C(SH) : NH$ , since this substance could neither retain the hydrochloric acid, nor afford mercaptan and yellow compounds of the metals named, but accord perfectly with the production of the hydrochloride of iminophenyl-carbaminethiomethyl [methyl iminophenylthiocarbamate], by loss of carbon dioxide from a group,  $MeO \cdot CO$ , attached to sulphur.



The hydrolysis with caustic alkali may be represented thus:



though, as indicated above, it does not occur quantitatively, inasmuch

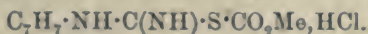
as a little sulphide is formed also ; the amount of change in this direction must be trifling, for not only is the desulphurisation imperfect, but when a direct experiment was made, by warming with dilute alkali and neutralising the solution with hydrochloric acid, a very small amount of precipitate was produced, in which no phenylthiourea could be detected ; the solution, however, reacted very markedly for thiocyanic acid, thereby proving that the weak alkali used was capable of effecting the hydrolytic change.

*Methyl Chlorocarbonate and p-Tolylthiourea.*

These constituents were treated as described for the preparation of the phenyl homologue and with similar results, except that a trifling effervescence took place after the mixture had remained for about half an hour ; when collected, washed, and dried, the product formed a yellow, apparently crystalline powder, the weight of which amounted to 98 per cent. of the theoretical. The solid was readily and almost completely soluble in cold water, yielding a very acid solution, which gave the reactions of a hydrochloride ; two concordant determinations of the combined hydrochloric acid, made by saturating the aqueous solution with normal alkali, showed it to be 13.7 per cent., whilst  $C_{10}H_{12}O_2N_2S$  would require  $HCl = 13.98$  per cent. During the addition of the alkali an oil separated, rapidly hardening ; the solid, when recrystallised from boiling alcohol, in which it is moderately soluble, was obtained in brilliant, flattened prisms, melting at  $175-176^\circ$  (corr.).

Analysis gave  $C = 53.8$  ;  $H = 5.8$  ;  $N = 12.6$  ;  $S = 14.8$ .  
 Calculated for  $C_{10}H_{12}O_2N_2S$ ,  $C = 53.52$  ;  $H = 5.53$  ;  $N = 12.53$  ;  $S = 14.3$  ;  
 $O = 14.3$  per cent.

Consequently, this compound is the homologue of that produced by similar treatment from phenylthiourea, namely :



When boiled with water or dilute hydrochloric acid, it scarcely dissolved, and the mixture gave with ferric chloride no colour change. But if heated with alkali and then acidified, a little hydrogen sulphide escaped, and the solution, when mixed with ferric chloride, now gave an intense reaction for thiocyanic acid.

Reverting to the observation that a slight effervescence occurred during the primary interaction, notwithstanding that this operation had been conducted in the cold ; it seemed likely that some of the thiomethyl compound had been formed owing to elimination of carbon dioxide, and this turned out to be the fact, for the hydrochloride, when

warmed with alkali, smelt faintly of mercaptan, and the liquor, when cooled and treated with lead acetate, gave a very well-marked yellow precipitate. As will be seen later, this decomposition occurs in certain cases so readily that thioalkyl bases alone can be obtained, even although moderate artificial cooling be applied.

*Methyl Chlorocarbonate and o-Tolylthiourea.*

The solid first became doughy, and presently frothed up into a vesicular mass, although the containing flask was continuously immersed in running water. Notwithstanding this intumescence, no considerable amount of gas was evolved, and in an hour or two the sponge hardened and became friable. When dry, the product formed a granular white powder, melting at 92–93°, with copious effervescence, and dissolving readily in water to a strongly acid solution. The combined hydrochloric acid was found to be 14.0 per cent., and a determination of nitrogen gave  $N = 10.96$  per cent.;  $C_{10}H_{12}O_2N_2S, HCl$  would require 13.98 and 10.78, respectively.

By the treatment with alkali, a solid was formed, which, as in the preceding cases, was free from chlorine, and yielded with excess of caustic alkali, which redissolves it, no odour of mercaptan; lead acetate, when mixed with the cooled liquor, gave no yellow precipitate, but the mixture was blackened on boiling. When recrystallised from alcohol, the solid separated in colourless prisms, melting, with copious effervescence, and the evolution of sulphuretted gas, at 175–176° (corr.).

On heating the aqueous solution of the hydrochloride, a white, crystalline solid was deposited, and some gas escaped, containing both carbon dioxide and hydrogen sulphide. All the hydrochloric acid had passed into the aqueous solution; the crystals were neutral, gave precisely the same reactions as those obtained by neutralisation of the cold solution of the hydrochloride, and when purified, melted at the same temperature as the latter; if the two products were mixed in equal proportions, the melting point remained unchanged.

When kept for about ten days exposed to air at the ordinary temperature, the hydrochloride showed marked signs of change; it had become pasty and vesicular, and although desulphurised by lead and silver salts, it now smelt decidedly of mercaptan when warmed with alkali, and hence was gradually becoming converted, by loss of carbon dioxide, into the  $\psi$ -base, already described (p. 556). By heating it on the water-bath, the change was quickly effected, the phenomena and results being similar in every way to those observed when the phenyl homologue was thus treated; the resultant base,



$C_7H_7 \cdot NH \cdot C(NH) \cdot SMe$ , after recrystallisation from dilute spirit, formed large, pure white crystals, melting at  $101-102^\circ$ , without effervescence.

*Methyl Chlorocarbonate and Allylthiourea.*

These substances interact readily, either alone or in presence of dry benzene; in a short time, however, decomposition commences, the mass liquefying, whilst carbon dioxide escapes, with formation of iminoallylcarbaminethiomethyl [methyl iminoallylthiocarbamate],  $AllNH \cdot C(NH) \cdot SMe$ . It was sought to preclude this change by keeping down the temperature, but decomposition soon commenced on removing the vessel from the freezing mixture. As no special interest attached to the isolation of an allyl derivative, the experiments were not further pursued.

*Thiourea and Chlorocarbonates.*

In the introductory portion of this paper, attention has been directed to the fact that ethyl chlorocarbonate, when uniting with thiourea, does not, as supposed by Pawlewski, afford ethyl thioallophanate,  $NH_2 \cdot CS \cdot NH \cdot CO_2Et$ , but yields instead a compound in which the sulphur is combined with a radicle derived from the chlorocarbonate. Judging from the preliminary qualitative examination to which the product was subjected in 1896, the radicle in question was inferred to be the carbethoxy-group; but in view of the information now acquired regarding the influence of temperature upon the course of these changes where monosubstitution derivatives are concerned, it became desirable to examine the interaction with special reference to the conditions under which it is brought about.

From what follows, it will be seen that, in this case also, the nature of the product depends upon the temperature at which it is formed.

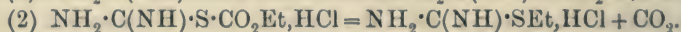
*Thiourea and Ethyl Chlorocarbonate.*—Complete interaction between these constituents at the ordinary temperature is not very easily effected in presence of benzene. Better results were obtained by adding the chlorocarbonate to the finely powdered thiourea, suspended in very gently warmed absolute alcohol; the latter reagent being only sparingly soluble, whilst the product dissolves readily, the completion of the process can be followed by the clearing of the mixture. Another method, for the suggestion of which the author is indebted to Mr. R. E. Doran, and which answers satisfactorily, is to treat the thiourea, suspended in absolute alcohol, with a slight excess of carbonyl chloride in toluene; the mixture clears immediately, and on slow evaporation,

colourless octahedral prisms separate consisting of the hydrochloride. When freed from a trace of oily matter by washing with a mixture of ether and alcohol, these melted sharply, with copious effervescence, at 116—117° (uncorr.), and hence were presumably identical with the substance described by Pawlewski (*loc. cit.*), who gives the melting point as 117°. The solid effervesced with sulphuric acid, giving off fumes of hydrogen chloride, and dissolved easily in cold water, yielding a highly acid solution; this remained clear when treated with excess of alkali, and did not smell of mercaptan, even if warmed; no yellow precipitate was produced on the addition of a lead salt to the mixture, but on boiling, desulphurisation occurred freely. Silver nitrate gave a white precipitate, consisting mainly of silver chloride; on treatment with ammonia this dissolved, and was replaced in the cold by a greenish-yellow one, which became black when the mixture was heated. A partial analysis was made.

Found S = 17.2; Cl = 19.3; N = 15.4.

$C_4H_8O_2N_2S.HCl$  requires S = 17.36; Cl = 19.21; N = 15.21 per cent.

Hence the compound is an additive product of thiourea and ethyl chlorocarbonate. When melted, it loses carbon dioxide only; the residue, if dissolved in water and mixed with excess of alkali, yields clear solution, smelling of mercaptan, and giving with a lead salt a bright yellow precipitate; the formation and decomposition of this compound by heat may thus be explained:



That is, thiourea and ethyl chlorocarbonate unite directly at or near the ordinary temperature to form a haloid salt of ethyl  $\psi$ -thio-allophanate; on heating, this is converted, by loss of carbon dioxide, into the corresponding salt of ethyl  $\psi$ -thiourea, otherwise imino-carbaminethioethyl (ethyl iminothiocarbamate).

By digesting the constituents together on the water-bath in presence of benzene, the latter compound was directly obtained, carbon dioxide being evolved, and eventually a clear, pale yellow syrup was left; this, when freed from benzene, &c., by heating for some time in an open dish, became viscid, but showed no tendency to crystallise. It was miscible with water, and the cold solution, when treated with alkali, smelt very foully of mercaptan; this mixture gave a clear yellow precipitate with lead acetate, and when dropped into ammoniacal copper sulphate, gave a black precipitate of copper cyanamide:



*Thiourea and Methyl Chlorocarbonate.*—Interaction was started by very gentle warming, care being taken not to heat the mixture enough

to cause the evolution of gas; it was left for several days, and the residue then collected. A white crystalline powder resulted, the weight amounting to 93 per cent. of the theoretical; when extracted by warm acetone, so as to remove any unchanged thiourea, it melted at 89—90° with copious effervescence, and gave the following percentages on analysis:

Found N = 16·8; S = 18·5; Cl = 20·65.

$C_3H_6O_2N_2S, HCl$  requires N = 16·47; S = 18·79; Cl = 20·78 per cent.

In this case, as in that of the ethyl homologue, direct titration of the combined hydrochloric acid proved unsatisfactory, the solution when apparently neutralised soon becoming acid again, so that a definite end point could scarcely be observed; the chlorine determinations given above were made by evaporating with pure caustic alkali, fusing the residue with nitre, and precipitating the acidified solution with silver nitrate.

The substance was freely soluble in water or alcohol, sparingly so in acetone, practically insoluble in chloroform or benzene. Its aqueous solution, if made just alkaline by caustic potash, and treated with a lead salt, gave no yellow precipitate, but the mixture was copiously desulphurised on heating; the compound, however, is rather unstable, for if boiled with water alone, carbon dioxide escapes, and the residual liquid when cooled and treated with alkali, has an odour of mercaptan, and now yields a yellow precipitate with a lead salt. A similar change occurs on melting, the effervescence being due to loss of carbon dioxide only, and the residue giving the mercaptoid reactions of a  $\psi$ -thiourea.

By allowing the same constituents to interact at the temperature of the water-bath, the usual phenomena were observed, the residue changing into an oil, which hardened on cooling to a white, crystalline hydrochloride, melting at 59—60°, and seemingly identical with the product obtained by fusing the substance prepared in the cold.

Found Cl = 27·8;  $C_2H_6N_2S, HCl$  requires Cl = 28·00 per cent.

The solid was easily soluble in water or spirit, yielding an almost neutral solution; when treated with cold alkali, this remained clear, but evolved mercaptan, and the mixture gave with lead salts a clear yellow precipitate, not desulphurised by heating. With warm ammoniacal silver nitrate a yellow precipitate formed, which, even on boiling, was scarcely perceptibly darkened, and hence was practically free from both thiourea and its carbomethoxy-derivative.



LXII.—*The Affinities of some Feebly Basic Substances.*

By JOHN KERFOOT WOOD.

SINCE the enunciation of the theory of electrolytic dissociation, a large amount of work has been done with a view to determining the strengths of acids and bases, these strengths or affinities being proportional to the extent to which the substances are ionised in aqueous solution. In the majority of cases, the desired object has been attained by determining the electrical conductivity of solutions of known strength, but for the so-called very weak acids and bases this method has been inapplicable, owing to the very slight dissociation which obtains in solutions of these substances. For such compounds as these, methods based on the catalysis or saponification of methyl acetate and the inversion of cane sugar have been employed, these methods being termed hydrolytic, because they are applied to substances the salts of which undergo hydrolysis in aqueous solution.

The present paper contains the results obtained in determining the strengths of a number of weak bases, many of which had not been previously examined from this point of view. These bases belong principally to the urea and uric acid series, and as their solutions are exceedingly poor conductors of electricity, the first of the above-mentioned hydrolytic methods was employed, namely, that dependent on the catalysis of methyl acetate.

The theoretical basis of the method has been set forth in an earlier paper, which also contains a full description of the mode of carrying out the determinations so as to secure the greatest possible accuracy (Walker and Wood, this vol., p. 484). In most cases the velocity constant of the solution of the hydrolysed salt was compared with that of a solution of acid and sodium chloride in proportions as nearly as possible the same as those existing between the free acid and the unhydrolysed salt in the former solution. The salts used were the hydrochlorides, and the solutions were prepared by adding to the base under examination sufficient normal acid to form a salt of the type  $B, HCl$ , and then diluting until the concentration was that of a  $N/10$  solution.

The experiments were carried out at a temperature of  $40.2^{\circ}$ , because in some cases solutions of greater concentration could be employed than would have been possible at lower temperatures, and, moreover, the experiments were rendered less protracted than they would otherwise have been.

The correctness of the determinations being largely conditioned by

the accuracy of the titrations, special care was taken to avoid error in this respect, a narrow glass tube carefully calibrated and mounted on a millimetre scale being used in place of an ordinary burette. The titrations were read in millimetres, actual volumes not being required for purposes of calculation. The tube was connected in the usual way with a reservoir containing barium hydroxide solution.

The observations are given in full in the case of urea, but with the other bases only the velocities of reaction are stated.

*Urea*.—Determinations of the hydrolysis of urea hydrochloride have already been made at 25° by Walker (*Zeit. physikal. Chem.*, 1889, 4, 337), and at 60° by Walker and Aston (*Trans.*, 1895, 67, 581). The urea, which was dried in a desiccator over  $\text{H}_2\text{SO}_4$ , melted at 130°.

*N/10 Urea Hydrochloride.*

| <i>t</i> . | Titre. | <i>x</i> .       | <i>A - x</i> . | <i>k</i> .      |
|------------|--------|------------------|----------------|-----------------|
| 0°         | 510·9  | 0                | 448·3          | —               |
| 180        | 356·4  | 154·5            | 293·8          | 0·001020        |
| 202        | 339·8  | 171·1            | 277·2          | 0·001034        |
| 236        | 318·9  | 192·0            | 256·3          | 0·001029        |
| 254        | 308·5  | 202·4            | 245·9          | 0·001027        |
| ∞          | 62·6   | <i>A</i> = 448·3 | —              | —               |
|            |        |                  |                | Mean = 0·001027 |

*N/10 Cl (90 per cent. HCl, 10 per cent. NaCl).*

| <i>t</i> . | Titre. | <i>x</i> .       | <i>A - x</i> . | <i>k</i> .      |
|------------|--------|------------------|----------------|-----------------|
| 0°         | 522·2  | 0                | 456·3          | —               |
| 183        | 362·5  | 159·7            | 296·6          | 0·001022        |
| 204        | 348·5  | 173·7            | 282·6          | 0·001021        |
| 233        | 327·5  | 194·7            | 261·6          | 0·001037        |
| 255        | 318·0  | 204·2            | 252·1          | 0·001010        |
| ∞          | 65·9   | <i>A</i> = 456·3 | —              | —               |
|            |        |                  |                | Mean = 0·001022 |

$$\text{Hydrolysis} = \frac{0\cdot001027}{0\cdot001022} \times 90 = 90\cdot4 \text{ per cent.}$$

*Thiourea*.—Determinations of the hydrolysis of the hydrochloride of this substance have already been made at different temperatures by Walker (*loc. cit.*) and Walker and Aston (*loc. cit.*).

The preparation used melted at 171°.

|  |                      |
|--|----------------------|
| <i>N/10</i> solution of thiourea hydrochloride.....          | <i>k</i> = 0·001115. |
| <i>N/10 Cl</i> solution (96 per cent. HCl, 4 per cent. NaCl) | <i>k</i> = 0·001061. |

These figures show that the salt is completely hydrolysed in *N/10* solution.

*Nitroguanidine*.—(Compare Jouselin, *Compt. rend.*, 1879, 88, 814 ; and Thiele, *Annalen*, 1892, 270, 15.)

The specimen used was prepared by Jouselin's method ;

0.0340 gave 15.3 c.c. moist nitrogen at 8° and 755 mm.  $N = 53.71$ .

$CH_4O_2N_4$  requires  $N = 53.84$  per cent.

Owing to its slight solubility, the hydrochloride was employed in  $N/25$  solution :

$N/25$  solution of nitroguanidine hydrochloride.....  $k = 0.0004290$ .

$N/25$  Cl solution (95 per cent. HCl, 5 per cent. NaCl).  $k = 0.0004180$ .

Hydrolysis = 97.5 per cent.

It has been stated in the previous paper (Walker and Wood, *loc. cit.*) that when the dilution of the solution varies, the hydrolysis of a solution in which the base and acid are in equivalent quantities is regulated by the equation

$$\frac{x^2}{(1-x)v} = c,$$

where  $x$  = amount of hydrolysed salt,  $(1-x)$  the unhydrolysed portion,  $v$  the volume, in litres, containing one gram-molecule of the substance, and  $c$  a constant.

Applying this equation to the case of nitroguanidine, it is found that a  $N/10$  solution of the hydrochloride would be hydrolysed to the extent of 94 per cent.

*Glycocyanine*.—A specimen of this substance was prepared from glycine and guanidine carbonate by the method described by Nencki and Sieber (*J. pr. Chem.*, 1878, [ii], 17, 747) :

0.0520 gave 15.75 c.c. moist nitrogen at 13.5° and 757 mm.  $N = 35.62$ .

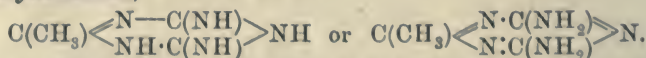
$C_3H_7O_2N_3$  requires  $N = 35.9$  per cent.

$N/10$  solution of glycocyanine hydrochloride .....  $k = 0.0001266$ .

$N/10$  Cl solution (10 per cent. HCl, 90 per cent. NaCl).  $k = 0.0001149$ .

Hydrolysis = 11 per cent.

*Acetoguanamine*,



—This substance, which was prepared by heating dry guanidine acetate at 230°, melted at 265° :

$N/10$  solution of acetoguanamine hydrochloride.....  $k = 0.0001160$ .

$N/10$  Cl solution (10 per cent. HCl, 90 per cent. NaCl).  $k = 0.0001180$ .

Hydrolysis = 9.8 per cent.

*Biuret*.—The sample employed, when recrystallised from alcohol and dried at 110°, melted at 189—190° :



|  |                 |
|--|-----------------|
| <i>N</i> /10 solution of biuret hydrochloride.....             | $k = 0.001140.$ |
| <i>N</i> /10 Cl solution (96 per cent. HCl, 4 per cent. NaCl). | $k = 0.001082.$ |

These figures show that the biuret hydrochloride is completely hydrolysed in *N*/10 solution :

|   |                 |
|---|-----------------|
| <i>N</i> /4 solution of biuret hydrochloride.....               | $k = 0.002850.$ |
| <i>N</i> /4 Cl solution (90 per cent. HCl, 10 per cent. NaCl).  | $k = 0.002595.$ |
| <i>N</i> /4 Hydrolysis in <i>N</i> /4 solution = 98.8 per cent. |                 |

*Semicarbazide*.—In this case the solution was prepared by dissolving the hydrochloride itself. The specimen employed after recrystallisation from alcohol melted at 174° :

|  |                  |
|--|------------------|
| <i>N</i> /10 solution of semicarbazide hydrochloride .....     | $k = 0.0001225.$ |
| <i>N</i> /10 Cl solution (10 per cent. HCl, 90 per cent. NaCl) | $k = 0.0001177.$ |
| Hydrolysis = 10.4 per cent.                                    |                  |

*Acetonesemicarbazone*.—The specimen was prepared in the usual way and melted at 184° :

|   |                  |
|---|------------------|
| <i>N</i> /10 solution of acetonesemicarbazone hydrochloride.    | $k = 0.0002948.$ |
| <i>N</i> /10 Cl solution (30 per cent. HCl, 70 per cent. NaCl). | $k = 0.0003284.$ |
| Hydrolysis = 26.9 per cent.                                     |                  |

*Creatine*.—The preparation used was analysed, with the following result :

0.0460 gave 12.75 c.c. moist nitrogen at 17.5° and 760 mm.  $N = 32.09.$   
 $C_4H_9O_2N_3$  requires  $N = 32.06$  per cent.

|   |                  |
|---|------------------|
| <i>N</i> /10 solution of creatine hydrochloride .....               | $k = 0.0001404.$ |
| <i>N</i> /10 Cl solution (13.4 per cent. HCl, 86.6 per cent. NaCl). | $k = 0.0001524.$ |
| Hydrolysis = 12.35 per cent.  |                  |

*Creatinine*.—A specimen of this base was kindly supplied by Prof. E. W. Reid, F.R.S. :

|   |                   |
|---|-------------------|
| <i>N</i> /10 solution of creatinine hydrochloride .....         | $k = 0.00009795.$ |
| <i>N</i> /10 Cl solution (10 per cent. HCl, 90 per cent. NaCl). | $k = 0.0001093.$  |
| Hydrolysis = 8.96 per cent.                                     |                   |

*Caffeine*.—The specimen which was analysed melted at 234° :

0.1717 gave 41.8 c.c. moist nitrogen at 11° and 759.5 mm.  $N = 28.84.$   
 $C_8H_{10}O_2N_4$  requires  $N = 28.67$  per cent.

Before preparing the solution the caffeine was heated at 130° in order to expel any water of crystallisation :

|   |                 |
|---|-----------------|
| <i>N</i> /10 solution of caffeine hydrochloride .....           | $k = 0.001015.$ |
| <i>N</i> /10 Cl solution (90 per cent. HCl, 10 per cent. NaCl). | $k = 0.001025.$ |
| Hydrolysis = 89.7 per cent.                                     |                 |

6-Aminocaffeine,  $\begin{array}{c} \text{N}(\text{CH}_3) \cdot \text{C}(\text{NH}_2) \cdot \text{C} \cdot \text{N}(\text{CH}_3) \\ \text{CO} - \text{N}(\text{CH}_3) - \text{C} = \text{N} \end{array} > \text{CO}$ .—This compound is precipitated by water from its solution in hydrochloric acid, and it has therefore been supposed to be a weaker base than caffeine, which is not liberated in this manner. As will be shown later, this precipitation of aminocaffeine cannot be taken as an indication that it is a very weak base.

The sample used was prepared by Fischer's method (*Annalen*, 1882, 215, 253):

0.0356 gave 10.4 c.c. moist nitrogen at 13° and 757 mm.  $\text{N} = 34.21$ .

$\text{C}_8\text{H}_{11}\text{O}_2\text{N}_5$  requires  $\text{N} = 33.49$  per cent.

On attempting to prepare a solution of the hydrochloride in the usual way, it was found to be impossible, owing to the very slight solubility of the base, to obtain a solution of sufficient concentration for conducting the experiments.

An approximate idea of the strength of a base can, however, be obtained by comparing its solubility in water with the solubilities in acid solutions of known strength.

The solubilities were determined by treating a known weight of the base with a definite volume of the solvent, the mixture being left in the thermostat for a day or two and vigorously agitated at intervals. The residue was then collected, thoroughly drained, and dried at 100°, the solubility being calculated from the weight of the undissolved base.

The following results were obtained:

100 c.c.  $\text{H}_2\text{O}$  dissolved 0.128 gram aminocaffeine.

100 c.c.  $N/20$   $\text{HCl}$  dissolved 0.192 gram aminocaffeine.

100 c.c.  $N/10$  „ „ 0.307 „ „

It has been shown by Walker (*loc. cit.*) that the hydrolysis equilibrium is governed by the law:

$$\frac{\text{Free base} \times \text{free acid}}{\text{Salt}} = C(\text{a constant}).$$

The data obtained in the solubility determinations indicate that, in the solution of aminocaffeine in  $N/10$  hydrochloric acid, the concentrations of the acid, aminocaffeine and aminocaffeine hydrochloride are respectively 0.09043-, 0.006125-, and 0.009567-normal. These figures show that the value of  $C$  is 0.0579, and since this constant has the same value for all systems containing the acid, aminocaffeine, and aminocaffeine hydrochloride, it is possible to calculate the amount of free base, that is, to ascertain the amount of hydrolysis, in a system containing equivalent amounts of aminocaffeine and hydrochloric

acid. The result calculated for the hydrolysis in a decinormal solution is 52.4 per cent. From the solubility of aminocaffeine in the *N*/20 acid a somewhat higher value is obtained. It may be considered therefore that the hydrolysis of aminocaffeine hydrochloride in decinormal solution is approximately 55 per cent. 6-Aminocaffeine therefore is a stronger base than caffeine; the precipitation produced on diluting the solution in hydrochloric acid is simply due to the slight solubility of the base in water, and is not to be regarded as giving any indication of the relative strength of the base.

*Theobromine*.—The specimen employed was analysed:

0.0794 gave 21.7 c.c. moist nitrogen at 13° and 743 mm.  $N = 31.42$ .

$C_7H_8O_2N_4$  requires  $N = 31.11$  per cent.

In this case also the hydrolysis of the hydrochloride was ascertained by the solubility method, which has already been employed by Theodor Paul (*Arch. Pharm.*, 1901, 239, 48) in determining this constant at 18°.

The following solubilities were obtained at 40.2°:

100 c.c. distilled  $H_2O$  dissolved 0.060 gram theobromine

100 c.c. *N*/20 HCl „ 0.074 „ „

100 c.c. *N*/10 HCl „ 0.0925 „ „

From the figures representing the solubility in  $H_2O$  and in *N*/10 HCl, the hydrolysis of theobromine hydrochloride in decinormal solution is calculated to be 71.7 per cent., whereas the value obtained from the *N*/20 solution is 74.1. The hydrolysis in a decinormal solution of theobromine hydrochloride is therefore approximately 73 per cent.

*Guanine*.—The purity of the specimen was ascertained by analysis:

0.1184 gave 47.0 c.c. moist nitrogen at 14° and 755.5 mm.  $N = 46.20$ .

$C_5H_5ON_5$  requires  $N = 46.35$  per cent.

The solubility method was also employed in this case:

100 c.c. distilled water dissolved 0.0039 gram guanine

100 c.c. *N*/10 HCl „ 0.0975 „ „

100 c.c. *N*/20 HCl „ 0.194 „ „

The calculated hydrolysis in a decinormal solution of guanine hydrochloride is 17.9 per cent.

*Xanthine*.—The base used was prepared by the action of nitrous acid on guanine:

0.1646 gave 52.2 c.c. moist nitrogen at 16° and 756 mm.  $N = 36.62$ .

$C_5H_4O_2N_4$  requires  $N = 36.84$  per cent.



The solubility method was employed:

100 c.c. distilled water dissolved 0.0183 gram xanthine.

100 c.c. *N*/10 HCl                      „    0.0210    „    „

The calculated hydrolysis in a decinormal solution of xanthine hydrochloride is 88.5 per cent.

*Acetoxime*.—Walker (*loc. cit.*) has shown that at 25° acetoxime is a stronger base than urea, and a similar result was obtained at the higher temperature employed in the present series of experiments. The sample used was prepared in the usual manner and melted at 61°:

*N*/10 solution of acetoxime hydrochloride .....  $k = 0.0003751$ .

*N*/10 Cl solution (35 per cent. HCl, 65 per cent. NaCl)  $k = 0.0003823$ .

Hydrolysis = 34.35 per cent.

*Acetamide*.—Previous experiments with this substance have been made by Walker (*loc. cit.*), and Walker and Aston (*loc. cit.*). The methyl acetate method employed in the former series of experiments showed acetamide to be slightly weaker than urea; in the other determinations, the method based on the inversion of cane sugar was used, and gave numbers showing urea to be the weaker base. The present experiments give a result in agreement with that previously obtained by the use of the methyl acetate method. The specimen employed melted at 82°:

*N*/10 solution of acetamide hydrochloride .....  $k = 0.001035$ .

*N*/10 Cl solution (90 per cent. HCl, 10 per cent. NaCl)  $k = 0.001020$ .

Hydrolysis = 91.3 per cent.

*Benzamide*.—M. p. 130°:

*N*/10 solution of benzamide hydrochloride .....  $k = 0.001106$ .

*N*/10 Cl solution (94 per cent. HCl, 6 per cent. NaCl)  $k = 0.001038$ .

These figures indicate that benzamide hydrochloride is completely hydrolysed in decinormal solution.

*Acetanilide*.—M. p. 115°. The hydrolysis was determined in a *N*/20 solution owing to the sparing solubility of the substance, and from the result obtained the value for a *N*/10 solution calculated, as in the case of nitroguanidine:

*N*/20 solution of acetanilide hydrochloride .....  $k = 0.0005215$ .

*N*/20 Cl solution (92 per cent. HCl, 8 per cent. NaCl)  $k = 0.0005112$ .

Hydrolysis: Found = 93.8 per cent.

Calculated for *N*/10 solution = 88.9 „

*Propionitrile*.—B. p. 96—97°. This substance has been shown to

possess feeble basic properties by Walker, and by Walker and Aston :

|   |                  |
|---|------------------|
| N/10 solution of propionitrile hydrochloride .....    | $k = 0.001088$ . |
| N/10 Cl solution (95 per cent. HCl, 5 per cent. NaCl) | $k = 0.001062$ . |
| Hydrolysis = 97.3 per cent.                           |                  |

*Dimethylpyrone*.—(Compare Collie, Trans., 1899, 75, 710). Earlier experiments conducted at 35° showed that the basic strength was about equal to that of urea (Walker, Ber., 1901, 34, 4115). The present determinations, made with dimethylpyrone hydrochloride kindly supplied by Prof. J. Norman Collie, F.R.S., show it to be a somewhat stronger base than urea :

|  |                   |
|--|-------------------|
| N/10 solution of dimethylpyrone hydrochloride .....    | $k = 0.0009033$ . |
| N/10 Cl solution (86 per cent. HCl, 14 per cent. NaCl) | $k = 0.0009142$ . |
| Hydrolysis = 85 per cent.                              |                   |

*Cyneol* is another non-nitrogenous substance, which unites with acids to form salts. A sample was obtained from oil of Cajeput by the method described by Wallach and Brass (*Annalen*, 1884, 225, 294). Owing to the slight solubility in water, the catalytic method could not be employed, whilst the value obtained by the solubility method can only be regarded as a rough approximation, because there is no accurate method for estimating cyneol. The method adopted was to mix known volumes of cyneol and water, or hydrochloric acid, and, after leaving the mixture for a day or two in the thermostat, observing the final volumes ; it was found that :

|  |      |
|--|------|
| 100 c.c. distilled water dissolved about 0.63 gram cyneol. |      |
| 100 c.c. N-HCl   | 0.79 |

As calculated from these solubilities, the hydrolysis in a decinormal solution would be about 98 per cent.

### Calculation of Dissociation Constants.

It was shown by Arrhenius (*Zeit. physikal. Chem.*, 1881, 5, 17) that the following equation holds for a system containing free acid, free base, and salt :

$$\frac{k_1}{k_2} = \frac{v(1-x)}{x^2},$$

where  $v$  = volume of solution, which would contain 1 gram-molecule of salt.

$x$  = the amount of hydrolysis calculated on 1 gram of salt.

$k_1$  = the affinity constant of the base.

$k_2$  = the affinity constant of water.

By means of this equation, therefore, it is possible to calculate the dissociation constants of the bases, the salts of which have been examined. The value of this constant for water is ascertained from Kohlrausch and Heydweiller's results (*Zeit. physikal. Chem.*, 1894, 14, 317); the amount of dissociation at  $40.2^\circ$  is  $1.775 \times 10^{-7}$ , giving a dissociation constant of  $1.775^2 \times 10^{-14}$ .

The hydrolysis of the hydrochlorides of the bases in decinormal solution and the calculated dissociation constants are given in the following table:

| Base.                     | Percentage hydrolysis<br>of hydrochloride in<br>decinormal solution. | Dissociation constant<br>of base at<br>$40.2^\circ$ . |
|---------------------------|--|---|
| Creatinine.....           | 8.9  | $3.57 \times 10^{-11}$                                |
| Acetoguanamine.....       | 9.8  | $2.96 \times 10^{-11}$                                |
| Semicarbazide.....        | 10.4   | $2.61 \times 10^{-11}$                                |
| Glycoeyamine.....         | 11.0   | $2.32 \times 10^{-11}$                                |
| Creatine.....             | 12.3   | $1.81 \times 10^{-11}$                                |
| Guanine.....              | 17.9   | $0.807 \times 10^{-11}$                               |
| Acetonesemicarbazone..... | 26.9   | $0.318 \times 10^{-11}$                               |
| Acetoxime.....            | 34.3   | $0.175 \times 10^{-11}$                               |
| 6-Aminocaffeine.....      | 55.0   | $0.047 \times 10^{-11}$                               |
| Theobromine.....          | 73.0   | $0.016 \times 10^{-11}$                               |
| Dimethylpyrone.....       | 85.0   | * $0.0065 \times 10^{-11}$                            |
| Xanthine.....             | 88.5   | $0.0046 \times 10^{-11}$                              |
| Acetanilide.....          | 88.9   | $0.0044 \times 10^{-11}$                              |
| Caffeine.....             | 89.7   | $0.0040 \times 10^{-11}$                              |
| Urea.....                 | 90.4   | $0.0037 \times 10^{-11}$                              |
| Acetamide.....            | 91.3   | $0.0033 \times 10^{-11}$                              |
| Nitroguanidine.....       | 94.0   | $0.0021 \times 10^{-11}$                              |

\* Walden (*Ber.*, 1901, 34, 4197), working at another temperature and employing a different method, has obtained a value for the dissociation constant of dimethylpyrone of the same order of magnitude as that given above.

It will be observed that the result obtained for the dissociation constant of urea is different from that previously given (Walker and Wood, this vol., p. 490), where the value is put down as  $0.0015 \times 10^{-11}$ . The discrepancy is due to the difference in temperature in the two cases, the experiments described in the earlier paper being conducted at  $25^\circ$ .

In addition to the bases mentioned in the table, the hydrochlorides of propionitrile, benzamide, cyneol, thiourea, and biuret were investigated and found to be more or less completely hydrolysed in decinormal solution. No attempt was made to calculate the dissociation constants of these bases, because no reliance can be placed on this coefficient when the amount of hydrolysis is greater than 95 per cent. Between 95 and 100 per cent. an error of 1 per cent. in



the hydrolysis is magnified to one of 50 or 100 per cent. in the dissociation constant.

As indicated in the following table, the calculated dissociation constants become more reliable when the hydrolysis is less :

| Hydrolysis.  | Dissociation constant.   | Change in hydrolysis. | Change in dissociation constant. |
|--------------|--------------------------|-----------------------|----------------------------------|
| 10 per cent. | $2.55 \times 10^{-11}$   | 10 per cent.          | 9.0 per cent.                    |
| 11    "      | $2.32 \times 10^{-11}$   |                       |                                  |
| 25    "      | $0.378 \times 10^{-11}$  | 4    "                | 9.5    "                         |
| 26    "      | $0.345 \times 10^{-11}$  |                       |                                  |
| 90    "      | $0.0039 \times 10^{-11}$ | 1.1   "               | 12.8   "                         |
| 91    "      | $0.0034 \times 10^{-11}$ |                       |                                  |

### *Discussion of Results.*

Five of the bases investigated, namely, guanine, xanthine, caffeine, 6-aminocaffeine, and theobromine, belong to the same series of compounds, and taking into account the general effects on the basic strength of a compound, caused by the introduction of amino- and methyl groups, it might be expected that the order of basic strength would be guanine, 6-aminocaffeine, caffeine, theobromine, and xanthine, guanine being the strongest base in the series.

A review of the results already given will show that this order is not strictly followed, the actual arrangement being guanine, 6-aminocaffeine, theobromine, xanthine, caffeine. The position occupied by caffeine is one to occasion surprise, but it has been confirmed by repeated experiments. Of these five substances, caffeine is the only one to which the methyl acetate method was applied, but the anomalous position of the base is not explicable on the grounds of differences in the methods of determination.

Solubility experiments made with caffeine showed that 100 c.c. of distilled water or *N*/10 HCl dissolve 4.463 or 4.755 grams of caffeine respectively. These solubilities give a hydrolysis of 86.1 per cent., a value which, whilst slightly below that found by the other method, is far too high to allow of caffeine taking a position between 6-aminocaffeine and theobromine. The result may possibly be explained by some singularity in the nature of caffeine, and the great difference between the solubility of this base and that of the other members of the series seems to support this view.

In the case of the urea and guanidine derivatives, perhaps the most surprising result is that given by biuret. Since ammonia is evolved in the course of its production from urea, it might be expected that

biuret would be slightly less basic than the parent substance. The results show, however, that biuret is practically devoid of basic attributes, a fact which could scarcely have been predicted from a consideration of the formula of the compound.

Another interesting result, obtained with nitroguanidine, illustrates the highly negative character of the nitro-group, for whereas guanidine has been shown by Bredig (*Inaug. Dissert. Leipzig*) to be a very strong base, the nitro-compound is a weaker base than urea.

The guanidine derivatives, glycoeyamine, creatine, and creatinine, are all weaker than guanidine and stronger than nitroguanidine.

Semicarbazide approximates in strength to these guanidine derivatives, and, as might be expected, is a much stronger base than urea.

Although the experiments have only been conducted at one temperature, it is scarcely probable that the order of affinity would be in any way changed if similar determinations were made at other temperatures. In the case of acetoxime, urea, acetamide, propionitrile, and thiourea, the order of basic strength at  $40.2^{\circ}$  is the same as that found by Walker with the same substances at  $25^{\circ}$ .

The author wishes to express his thanks to Prof. Walker, F.R.S., for the kindly advice and encouragement which he has given during the progress of this investigation.

UNIVERSITY COLLEGE,  
DUNDEE.

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### LXIII.—*Reversibility of Enzyme or Ferment Action.\**

By ARTHUR CROFT HILL, M.A., M.D.

#### *Introductory.*

IN an account of some former experiments communicated to the Chemical Society (Trans., 1898, 73, 634), I showed that the hydrolysis of maltose to glucose by yeast maltase in concentrated solution was incomplete, and that the phenomenon was due to polymerisation of the glucose by a reversible process, so that in solutions of maltose or glucose or of the mixed sugars, synthesis and hydrolysis took place until the system approached a state of chemical equilibrium, the equilibrium point being a function of the concentration of the solution.

\* This contribution formed a part of a thesis entitled "The process of chemical synthesis in living things," presented for the M.D. degree in the University of Cambridge.

The amount of change in these experiments was measured by the alterations in optical activity and in cupric reducing power, and the results were stated in terms of the conversion of maltose into glucose and of glucose into maltose, although, as I ascertained subsequently, the products of the synthetical action include one other sugar at least (Proc., 1901, 17, 184). Maltose, as a product of the synthetical action, was not itself isolated, but by treating the total products of the synthetical action on glucose with phenylhydrazine, a mixture of osazones was obtained, from which, on fractionation, a small quantity of an osazone was separated, which, although not quite pure, resembled maltosazone, and was shown to be the osazone of a biose.

In the first stage of polymerisation of glucose, a large number of isomeric bioses are conceivably possible, but one would expect that with any particular enzyme, or group of enzymes, only those would be formed which are capable of being hydrolysed back to glucose by the same enzyme; further, of such substances formed, only those would be found at the end of the reaction which are in equilibrium with the other reacting substances when in appreciable concentration, and the higher the initial concentration of the glucose the larger might be the number of such substances in appreciable concentration at the end. Again, other conditions being equal, an increase in the variety of enzymes would increase the total amount of glucose changed.

I have obtained experimental evidence bearing on these points with yeast-extract, taka-diastrase, and with the enzymes of pig's pancreas respectively. The products of the synthetical action were not completely identical in these cases. The differences might be due to one or more of the following causes:

(i) Specific differences in the enzymes; for example, the maltase of yeast extract being different from that of taka-diastrase.

(ii) Difference in the variety of enzymes present.

(iii) Difference in the proportion of enzymes present.

With regard to yeast-extract and taka-diastrase, the second and third factors seem to have been chiefly effective.

In every instance, on diluting the products of the synthetical action, it has been found possible to hydrolyse them back to glucose by the enzyme used in their synthesis. Further, the synthetical products of the action with yeast-extract were capable of hydrolysis by taka-diastrase, and those of the action with taka-diastrase by yeast-extract. Preliminary notes on these results have been published [taka-diastrase and reversed ferment-action (Proc., 1901, 17, 184); synthetical action on glucose with pancreatic ferments (*Proc. Physiol. Soc.*, 1902, 28, xxvi)]. Although it is likely, or at any rate possible, that maltase acting on glucose may produce isomerides, it is not proved that by itself it can produce anything but maltose, as it has hitherto been impossible to



obtain it free from other enzymes. In fact, in making a preparation of any enzyme, it is never possible to exclude admixture with unknown enzymes, although particular ones may be excluded. That a considerable part of the synthetical product obtained by the action of yeast extract on concentrated glucose solution is possibly formed by the agency of enzymes other than maltase is suggested by fermentation experiments. *Saccharomyces Marxianus* is a yeast which, as was discovered by Hansen in 1888, ferments glucose, but not maltose. I made use of this yeast in 1900 for separating maltose from glucose in mixtures of these two sugars, and published a note on the details of the method (Proc., 1901, 17, 45). If the product obtained by the action of yeast extract on concentrated glucose solutions, including thus the synthetical product and the unchanged glucose, is fermented with *S. Marxianus*, only the unchanged glucose is fermented. If, on the other hand, one ferments with a maltase-containing yeast—and I have tried several varieties, each in a pure culture—not only is the glucose fermented, but also a part of the synthetical product, the larger portion, however, which is not maltose, being unattacked. If, lastly, the product after dilution is hydrolysed, first with some yeast-extract, similar to that used in its formation, it is then fermented completely by *S. Marxianus*. Evidence has been obtained that the smaller portion of the synthetical product, which is fermented by maltase-containing yeasts, consists of maltose or a mixture of this biose and higher polymerides. The larger portion, however, which is unfermented unless previously hydrolysed, has optical and reducing properties between those of maltose and of glucose. It consists mainly of a biose which is not identical with any known sugar and which I have called *revertose*. I have avoided the name *isomaltose* because this designation has been applied to several differing substances, and *revertose* is different from any of these. The question then arises, is *revertose* formed by maltase or by another enzyme in the yeast extract.

Fermentation experiments, on the one hand, might seem to show that the yeast-extract, which is prepared from dried Berne yeast, contains an enzyme capable of synthesising *revertose*, but that this is not available in the fresh maltase-containing yeasts, and is distinct therefore from maltase. Another possible explanation is that when maltose is fermented by a maltase-containing yeast, the splitting probably takes place intracellularly and the conditions of equilibrium prevailing within the cell may be much more favourable for the splitting of maltose than for the splitting of *revertose*; they must be somewhat so, as on comparing the equilibrium of maltose  $\rightleftharpoons$  glucose with that of *revertose*  $\rightleftharpoons$  glucose in 40 per cent. sugar solutions, it is seen that the splitting of maltose is much nearer completion, or, looking at it from the synthetical point of view, a much smaller

quantity of maltose is formed than of the other biose. The equilibrium of maltose with glucose is the more favourable for hydrolysis, that of revertose with glucose for synthesis.

The products obtained by the action of taka-diastrase on 60 per cent. glucose solutions have not been separated. The quantity of glucose converted is actually greater than it appears to be when stated in terms of its conversion into maltose (Proc., 1901, *loc. cit.*), as the optical activity and cupric reducing power of the mixed synthetical products lie between those of maltose and those of glucose. This is true both of the products obtained with yeast extract and with taka-diastrase, and will be dealt with in this paper, but in the case of the latter there are also other products not yet investigated which diminish the optical activity of the total products.

Fermentation experiments with the synthetical products of the taka-diastrase action show that, just as with the products of yeast-extract, a portion not fermented by *S. Marxianus* is, nevertheless, fermentable by maltase-containing yeasts, the remainder not being directly fermented even by these. The change effected by pancreatic extract in 60 per cent. glucose solutions was small and probably incomplete on account of the destruction of maltase by trypsin. It was verified, however, after subsequent fermentation of the unaltered glucose with *S. Marxianus*.

### EXPERIMENTAL.

The methods used in these experiments were substantially the same as those previously described (Trans., *loc. cit.*). The glucose was purified as before and the yeast extract prepared in the same way, the yeast being obtained from the same brewery. It was noted that when the powdered yeast had been dried for a considerable time *in vacuo* over sulphuric acid at 15°, it yielded an extract approximately as active as if the powder had been heated after the drying in the manner described in my former paper, and the loss of weight on heating, when the drying at 15° has been thus prolonged, is trifling. This indicates that heating the powder increases its activity only by rendering the drying more efficient. For the supply of taka-diastrase, I am indebted to Messrs. Parke, Davis, & Co., and for the extract of pig's pancreas to Mr. Benger.

The method of conducting the fermentations was similar to that already described for the separation of maltose from glucose (Proc., 1901, *loc. cit.*). The pure cultures of the various yeasts were all obtained from Dr. Kral, Prague, and recultivated, with usual bacteriological precautions, in broths containing sugar until a sufficient quantity of each was obtained. In the cultivation of *S. Marxianus*



glucose was the only sugar in the nutrient medium; for the maltase-containing yeasts, maltose was also added. The yeast was then washed with sterilised tap-water on the centrifuge before being added to the sugar solutions it was desired to ferment.

No addition of nutrient salts was made, excepting such as might be present in the tap-water which was used for diluting the concentrated solutions. To render the fermentation as complete as possible, however, it was allowed to proceed at about 15°, usually for several weeks. The synthesised sugars formed from glucose by yeast extract were obtained in the following way. After fermentation of the unchanged glucose with *S. Marxianus*, the fermented fluid was evaporated on the water-bath under diminished pressure while a current of dried carbon dioxide was passed through it, ethyl alcohol being added from time to time. The syrup was then poured into boiling ethyl alcohol, the hot solution being filtered from the precipitate, which consisted, to a large extent, of salts, but contained also a little dextrin and substances from the yeast-extract. On cooling, the alcoholic filtrate deposited a syrup, the yield of which was increased by allowing the solution to stand over lime or anhydrous cupric sulphate in desiccators. The various fractions obtained in this way were analysed, as well as the precipitates and final mother-liquors. The syrup obtained was then again fractionated with alcohol.

When *S. Ellipsoideus I*, which ferments maltose and glucose, was used instead of *S. Marxianus*, the syrup obtained in this way could not be further fractionated; that is to say, the optical activity and optical factor for all the fractions excepting the most insoluble and the final mother liquor were alike, showing that only one sugar remained. When the syrup containing this sugar is left over lime, it becomes first a glassy solid, and later, opaque and crystalline. It is the sugar I have named revertose, and its properties will be described later. The syrup obtained, however, after fermentation with *S. Marxianus*, could always be further fractionated, and contained both revertose and another biose of higher optical activity. The fractions, soluble in increasing strengths of alcohol, contain progressively more of this biose and less of revertose, and their optical and other properties approach those of maltose.

The polarimeter used was the one previously described, and the cupric reduction value of the sugars was also determined in the same way as previously, excepting that the ammoniacal cupric solution contained more caustic alkali. It has been prepared from Fehling's solution, having the formula given in the last edition of the "British Pharmacopœia"; this makes the value of  $R$  for maltose hydrate, 40 (glucose = 100), whereas in my former paper the value was 38; the constant  $R$  for anhydrous maltose is of course 5 per cent. higher.



The progress and results of my early experiments with yeast-extract on maltose and glucose solutions were stated in terms of the conversion of maltose to glucose and of glucose to maltose, but having found that the reaction was less simple and that one other sugar at least was present in the end product, I have since recorded the changes in optical activity and reducing power by a single factor which has been of considerable convenience. It is the ratio of the optical activity to reducing power or  $\frac{[\alpha]_D}{R}$  (taking  $R=100$  for glucose), and is called in this paper the *optical factor*.

The optical factor for glucose (rotation taken in 2 per cent. solution) is 0.525.

The optical factor for maltose (rotation taken in 1 to 2 per cent. solution at  $15^\circ$ ) is 3.275,

that is, more than six times as great. The optical factor for revertose is intermediate, 1.91 or 1.92. It is to be noted that the values depend on  $R$ , and therefore except in the case of glucose ( $R=100$ ) will be different for different copper solutions, that is, considerably less for maltose with the direct use of Fehling's solution. The great advantage of the factor is that it can be written down for any sugar or mixture of sugars in solution directly from the optical and reducing properties as measured, although the specific optical and reducing properties are unknown, that is, when the concentration has not been determined. For, let

$\alpha_D$  = the observed rotation for ( $D$ ) ray in 200 mm. tube,

$\rho$  = the reducing power in terms of that of a standard 0.2 per cent. glucose solution,

And  $C$  = the concentration (unknown),

then the optical factor is

$$\frac{[\alpha]_D}{R} = \frac{\alpha_D \times 50}{C} \div \frac{\rho \times 100 \times 0.2}{C} = \frac{5\alpha_D}{2\rho}.$$

#### *Experiments with Yeast Extract.*

In experiment VIII of a former paper (Trans., 1898, 73, 652), the effect of yeast-extract on 40 per cent. glucose solution was given. The change in optical activity corresponded with a change of 14 per cent. of the glucose to maltose hydrate, and the alteration in cupric reducing power corresponded with a change of 15 per cent.; in another flask, the values obtained were 14.5 per cent. and 15.5 per cent. respectively. The changes, therefore, in optical and reducing properties corresponded fairly on the assumption that there was a conversion of glucose to maltose, although the alteration in reducing power was in slight excess. I have since repeated the experiment

several times with identical results. This correspondence must now be regarded as a coincidence, for, as I have pointed out in other publications, the product of the synthetical change is less simple than at first appeared probable. In these experiments, the optical factor is raised from 0.525, the factor for glucose, to 0.68 (0.70 with the copper solution used in my earliest experiments).

In resuming the work about three and a half years ago, with a view to isolating the synthetical products, I experimented first with *S. Marxianus* and satisfied myself that it fermented glucose efficiently in mixtures of glucose and maltose and did not attack the latter sugar. It was then used as follows. The products of the action of yeast-extract on 40 to 45 per cent. solutions of glucose, having an optical factor of 0.68, were diluted with sterilised tap-water four times (in some instances eight times) and fermented with *S. Marxianus*, and the optical factor was thereby raised to 2.20 or 2.25. The factor was not appreciably altered by extracting the solution with ether, and it was considerably lower than that of maltose (3.275).

It seemed possible at first that a mixture of maltose and glucose was left behind. The residue did not crystallise from alcoholic solutions, but separated as a syrup, whilst, as I also found, an attempt to crystallise maltose and glucose from an alcoholic solution containing the two sugars in equal parts results in the formation of a hygroscopic, uncrystallisable mixture. However, in fermentation experiments of mixtures of maltose and glucose, it was apparent that in such a mixture, under suitable conditions and when the fermentations are continued for several weeks, this yeast will destroy 99.8 per cent. of glucose without attacking the maltose, and that it is quite easy to recover more than 80 per cent. of the maltose at once in a pure, crystalline state, even when only 94 per cent. of the glucose has been fermented (Proc., *loc. cit.*), so that clearly in the reversion experiments, one had to do with something else than a simple mixture of maltose and glucose. Further evidence of a similar nature was obtained in reversion experiments with taka-diastase and a note on the point was published (Proc., 1901, *loc. cit.*).

#### *Hydrolysis of the Reversion Products.*

There was no doubt, however, that the synthetical product was formed by a reversible process, for it was again hydrolysed by the same ferment in dilute solution, and it had therefore been necessary in my original experiments on reversion to destroy the ferment before diluting the solution in order to fix the synthetical product. But the enzyme is then attenuated, and hydrolysis of the synthetical product is better shown by adding fresh ferment to the dilute solution as in the

following experiment. The material which was produced by acting on a 45 per cent. glucose solution with yeast-extract until the optical factor had been raised from 0.525 to 0.80 had been subsequently boiled and the optical factor as determined at the beginning of the experiment was 0.676.

### Experiment I.

Flask *A*, containing 10 c.c. of the solution (optical factor, 0.676), 10 c.c. of active yeast-extract diluted with water to 200 c.c., with an addition of two drops of toluene, was placed in the thermostat at 28° together with a control flask, *B*, containing the same mixture, but with the ferments destroyed by heat.

After 10 days, the optical factors in *A* and *B* were 0.537 and 0.675 respectively. The hydrolysis in *A* was nearly complete.

The contents of each flask, after the addition of an equal bulk of *S. Marxianus*, were then fermented for 2 weeks, adjusted to the original volume, and examined:

#### In *A*.

|  | Before<br>fermentation. | After<br>fermentation. | Optical<br>factor. |
|--|-------------------------|------------------------|--------------------|
| Optical activity of the solution<br>in 200 mm. tube..... | 2.37°                   | 0.13°                  | 1.3                |

#### In *B*.

|  |      |      |     |
|--|------|------|-----|
| Optical activity of the solution<br>in 200 mm. tube..... | 2.75 | 0.80 | 2.1 |
|--|------|------|-----|

The synthetical products, therefore, on dilution were hydrolysed back again by the same ferments that had produced them and were then fermentable by *S. Marxianus*, whilst in the control flask no hydrolysis took place, and this also was confirmed by fermentation. The residual optical activity in *B* (0.80°) was more than six times that in *A* (0.13°), whilst the optical factors, which increased throughout the fermentations, show that the difference was not due to incomplete fermentation in *B*.

The synthetical products obtained by the yeast-extract are also hydrolysed by taka-diastase.

### Experiment II.

Flask *A* contained 10 c.c. of the same solution as in Exp. I, thrice boiled (optical factor, 0.673), 5 c.c. of 10 per cent. solution of taka-diastase diluted with water to 100 c.c. Flask *B* (control) containing the same mixture, but the taka ferments were destroyed by heat.



A few drops of toluene were added to each flask, which was then placed in a thermostat at 28°.

In *A*, the optical factor at the start was 0·673, and decreased to 0·613 and 0·588 after 5 and 11 days respectively. In *B*, the optical factor after 11 days was 0·669.

The hydrolysis of the synthetical products after isolation is well shown by the following experiment :

*Experiment III.*

| Flask <i>A</i> .   |         |             |   | Flask <i>B</i> .   |         |             |   |
|--|---------|-------------|---|--|---------|-------------|---|
| 2·6 grams revertose (the product of the action of yeast-extract on glucose separated after fermentation with <i>S. Ellipsoideus I</i> ). |         |             |   | 2·4 grams mixed synthetical bioses (the product of the action of yeast-extract on glucose separated after fermenting with <i>S. Marxianus</i> ). |         |             |   |
| 0·2 grams taka-diasatase   |         |             |   | 0·2 grams taka-diasatase   |         |             |   |
| Water to 100 c.c.  |         |             |   | Water to 100 c.c.  |         |             |   |
| Optical activity of <i>A</i> at the start  |         |             |   | Optical activity of <i>B</i> at the start  |         |             |   |
|  |         | 4·81° D ray |   |  |         | 4·65° D ray |   |
| after  | 4 days  | 4·51        | „ | after  | 4 days  | 4·05        | „ |
| „  | 10 „    | 4·21        | „ | „  | 10 „    | 3·72        | „ |
| „  | 4 weeks | 3·76        | „ | „  | 4 weeks | 3·24        | „ |
|  |         |             |   | „  | 8 „     | 2·80        | „ |

The initial and final values of the optical factor of *B* were 2·31 and 0·756 respectively. It will be noticed that at the very beginning the change in *B* was much the more rapid, the diminution in optical activity between the first two observations being exactly double that in *A* ; afterwards, the hydrolysis in the two flasks proceeded at equal rates. The explanation is probably to be found in the fact that maltose is hydrolysed more rapidly than revertose, flask *A* containing the latter sugar only.

*Fermentability of a Part of the Synthetical Product.*

Some of the same solution as used in Experiments I and II was utilised in these fermentation experiments, all this part of the work being done in 1901. The selected yeast was cultivated, washed, &c., as previously described, and added to the above solution diluted with tap-water to four times the original volume, excepting where a different dilution is stated. After the fermentations, the solutions were filtered, first through paper and then through porcelain, and the optical factor was determined. When the "residual opticity" is stated, allowance is made for evaporation, so that the figures for

each fermentation experiment are as nearly as possible comparable one with the other. All the yeasts used, with the exception of *S. Marxianus*, were maltose-fermenting yeasts :

| Variety of yeast used.     | Solution diluted before fermentation. | Length of fermentation. | Optical factor before fermentation. | Optical factor after fermentation. | Residual opticity. | Equivalent for four times diluted. |
|----------------------------|---------------------------------------|-------------------------|-------------------------------------|------------------------------------|--------------------|------------------------------------|
| <i>S. Marxianus</i> .....  | 4 times                               | { 1 month               | 0·67                                | 2·22                               | 3·40               | 3·40                               |
|                            |                                       | { 2½ "                  | 0·67                                | 2·28                               | 3·16               | 3·16                               |
| <i>S. Cerevisia</i> Saaz   | 4 "                                   | { 1 "                   | 0·67                                | 1·975                              | 3·12               | 3·12                               |
|                            |                                       | { 2½ "                  | 0·67                                | 1·965                              | 2·26               | 2·26                               |
| <i>S. Marxianus</i> .....  | 2 "                                   | 1 "                     | 0·67                                | 2·225                              | 6·95               | 3·47                               |
| <i>S. Ellipsoideus</i> I.. | 8 "                                   | 6 weeks                 | 0·675                               | 1·92                               | 1·65               | 3·30                               |
| <i>S. Carlsberg</i> I. ... | 8 "                                   | { 6 "                   | 0·675                               | 1·92                               | 1·76               | 3·52                               |
|                            |                                       | { 3 months              | 0·675                               | 1·955                              | 1·50               | 3·00                               |
| <i>S. Logos</i> .....      | 8 "                                   | 6 weeks                 | 0·675                               | 1·96                               | 1·52               | 3·04                               |

It is to be noted that the optical factor rises throughout the fermentation as the glucose disappears, the mean optical factor in a number of less prolonged fermentations with *S. Marxianus* being 2·19. Extraction of the solutions with ether was practised in several instances, but without materially altering the optical factor. A few other maltose-fermenting yeasts, including *S. Cerevisia* Froberg, were tried with a similar result. The conclusion from these experiments is :

(i) That a small part of the total synthetical product of yeast-extract on glucose is fermentable by all maltose-fermenting yeasts, and consists probably of maltose and its higher polymerides.

(ii) That the larger part, which I have found to include another biose, namely, revertose, is not fermented by all maltose-fermenting yeasts, but seems to be slowly attacked by some.

#### *Analysis of the Synthetical Products obtained from Glucose by the Action of Yeast-extract.*

These products have been examined after fermentation with (1) *S. Ellipsoideus* I, (2) *S. Marxianus*. The material for the separation of revertose was obtained by acting on 300 grams of glucose in a 45 per cent. solution with the extract of 6 grams of dry yeast powder until the optical factor was raised from 0·525 to 0·682. It was then diluted 4 times with tap-water and fermented with *S. Ellipsoideus* I, until the optical factor was raised to 1·99, afterwards filtered and evaporated in the manner already described, and poured into boiling

ethyl alcohol in such proportion as to form 400 c.c. of a 60 per cent. alcoholic solution.

*Fraction I*, the precipitate that first separated, was found to consist of salts and albuminoid substances from the yeast-extract, together with a little dextrin and sugar. The part of this precipitate soluble in water weighed 0.53 gram, of which 0.03 was ash, and it had the following properties:  $[\alpha]_D$  and  $R$  of the solids less ash are 81 and 15.7 respectively, the optical factor being 5.15.

This factor shows the presence of a substance having an optical factor higher than that of maltose, probably dextrin. The yeast-extract used in these experiments contained a little diastase, and the synthetical action had in these cases been allowed to proceed for many months. The difference in optical factor between the solutions after fermentation by *S. Ellipsoideus I*, on the one hand, and some of the beer yeasts on the other, may be due to fermentation of dextrin by the latter; the larger difference in residual opticity shown after prolonged fermentation by *S. Cerevisiae Saaz* and some other yeasts may be occasioned by a slow fermentation of revertose. The above-mentioned alcoholic solution was filtered hot; there was a separation of syrup on cooling, and the whole was then left over lime in a desiccator, by which means the strength of alcohol was increased. The following other fractions were separated in the order named.

*Fraction II*, a good deal of which separated when the alcoholic filtrate first cooled, was by far the largest. It consisted of a vitreous, sticky, yellow mass, which afterwards became opaque and crystalline when left for a long time in the desiccator. It contained 1 per cent. of ash and had  $[\alpha]_D$  89.5° and  $R$  47', reckoned on the total solids minus ash, with an optical factor 1.90.

*Fraction III* separated from the mother-liquor of the last fraction after further dehydration in the desiccator.

Its appearance was similar to that of fraction II. The total solids, less ash, had  $[\alpha]_D$  91°,  $R$  47.5, with an optical factor 1.91.

*Fraction IV* was a precipitate obtained by adding absolute alcohol to the mother-liquor from fraction III, the solids, less ash, had  $[\alpha]_D$  90.5°,  $R$  44.5, and optical factor 2.00.

*Mother liquor* from fraction IV. The solids, less ash, had  $[\alpha]_D$  76.5°,  $R$  38, and optical factor  $2.00 \pm 0.04$ .

It will be noticed that in all the fractions but the first precipitate and the final mother liquor, which both necessarily contain substances other than sugars, there was a remarkable uniformity in the analytical results obtained, justifying the inference that only one sugar is concerned. This sugar is shown to be a biose by a combustion of its osazone, and is the one I have called revertose.



*Revertosazone.*

Twenty-six grams of the sugar, obtained as above, were heated with phenylhydrazine hydrochloride and sodium acetate on the water-bath in the usual way, and the crystals which separated on cooling were washed with water, alcohol, and ethyl acetate, then collected, and recrystallised from ethyl acetate.

Results of analysis: Found, C=55.9; H=6.0; N=11.3.

Calculated for the osazone of a biose, C=55.4; H=6.1; N=10.8 per cent.

The osazone was not yet quite pure and its melting point was not sharp. It was therefore carefully recrystallised from ethyl acetate and the nitrogen determined:

Found, 10.8. Calculated, 10.8 (10.77) per cent.

The melting point was considerably raised and much sharper, 173—174° (corr.). The osazone, which crystallises in yellow needles, is optically inactive and thus readily distinguished from Fischer's isomaltosazone, the latter having an optical activity  $[\alpha]_D +7^\circ$  (Ber., 1895, 28, 3027). A 4 per cent. solution in ethyl alcohol containing a small quantity of ethyl acetate was prepared and examined with the arc light in a 100 mm. tube; no optical activity could be detected, although, under these conditions, a rotation of  $0.05^\circ$  would certainly have been noticed. The osazone is therefore optically inactive or has a specific rotation much smaller than  $\pm 1^\circ$ . A 2 per cent. solution in 50 per cent. alcohol had previously been examined in monochromatic light with a similar result.

Revertose itself is a hygroscopic sugar which has only been obtained crystalline by dehydrating the vitreous sugar, either slowly in a desiccator over lime, sulphuric acid, or anhydrous cupric sulphate, or, on the other hand, by heating *in vacuo*, when it loses water and becomes crystalline; this takes place at  $100^\circ$ , but much more rapidly at  $110^\circ$  or  $115^\circ$  in a glycerol bath. The sugar, which has not been obtained in detached crystals, has a sweet taste; its optical and reducing properties are as follows:  $[\alpha]_D +91.5^\circ \pm 1^\circ$ , and  $R$  47.5. Its optical factor is thus about 1.92. It will be noticed that its specific rotation is at least  $16^\circ$  higher than that of gallisin (Schmitt and Cobenzl, Ber., 1884, 17, 1007) and about  $48^\circ$  lower than the isomaltose of Lintner. It differs even more widely in optical properties from both gentiobiose and cellose. In short, I have not been able to identify it with any biose hitherto described, although it is likely to be present in certain beers and other fermented liquors. It would be of some interest to ascertain whether it also occurs in the animal system.

*Maltose.*

In my paper communicated to the Chemical Society in 1898 (*ibid.*), a description was given of the separation of an osazone resembling maltosazone when not quite pure. This product crystallised in aggregates of plates and gave on combustion, numbers corresponding with the osazone of a. biose. Its melting point, however, was not constant and the values given varied from  $173^{\circ}$  up to  $186^{\circ}$ . Maltosazone, when pure, melts at  $206^{\circ}$ , and there can be but little doubt that it was the presence of a certain proportion of the isomeric revertosazone which affected the melting point.

I have not been able to find a yeast which ferments revertose without fermenting maltose, nor should I expect to do so, consequently I have not been able to prove the formation of maltose as conclusively as if the sugar itself could have been isolated in a state of purity. It has been found possible, however, by fractionating mixtures of the two bioeses, to obtain products with an  $[\alpha]_D$  as high as  $120^{\circ}$  or even somewhat higher. Further, I have shown that the fermentation test for the presence of maltose is positive. This is seen by comparing the fractions separated after fermentation with *S. Marxianus* with those fermented with *S. Ellipsoideus I*. Thus, after *S. Marxianus* and alcoholic fractionation, a large fraction is obtained with the following properties:  $[\alpha]_D$   $98^{\circ}$ ,  $R$  42.5, optical factor 2.31. A higher fraction soluble in stronger alcohol gave  $[\alpha]_D$   $115^{\circ}$ ,  $R$  49.3, optical factor 2.33, whilst further fractions separated from the strongest alcohol gave the following values:

- |       |              |                 |     |    |                |      |
|-------|--------------|-----------------|-----|----|----------------|------|
| (i)   | $[\alpha]_D$ | $119.7^{\circ}$ | $R$ | 52 | optical factor | 2.30 |
| (ii)  | "            | $120^{\circ}$   | "   | 51 | "              | 2.35 |
| (iii) | "            | $120^{\circ}$   | "   | 52 | "              | 2.31 |

The sugars separate from the strongest alcohol as white, opaque solids, instead of the syrup or transparent solid obtained from alcohol of lower strength. It is to be noted in these higher fractions that, although the specific rotation approaches that of maltose, yet the reducing power is greater than in the lower fractions, and consequently the optical factor cannot be raised much above 2.35—the highest I have obtained is 2.38. Such a result may be due to traces of glucose, which would all appear in the highest fractions, for example, a mixture of about 4 parts of maltose with one of glucose would give the values found, and it is to be noted that *S. Marxianus* is less efficient than *S. Ellipsoideus I* in removing the last traces of glucose under the conditions of my fermentations. The fractions in question were too small to analyse further, but doubtless also contain a little revertose.

The osazone from these fractions, itself fractionated as described in my former paper, yields a product crystallising in plates which resemble those of maltosazone.

The identity of the second biose is therefore not rigidly established, but there can, I think, be very little doubt about its being maltose. It is, perhaps, hardly necessary to point out that the identity of this sugar is not relevant to the question of the reversibility of its formation. Although it is necessary to the theory that some maltose should be formed when maltase is present, it is by no means necessary that the quantity formed and remaining at the end of the reaction should be sufficiently large to be recognised, and it would be quite consistent with the theory that this sugar, formed as it is by a strictly reversible process, should be another isomeric biose. There is, however, nothing in any of the tests I have as yet been able to apply, either analytically or by fermentation, by which I can distinguish it from maltose. Not more than about one part of this sugar to five parts of revertose is formed, but the total amount of glucose changed in 41 per cent. solution by yeast-extract is nearly twice that calculated, as in my early papers, in terms of a conversion of glucose to maltose only. In all probability, more maltose is formed in the reaction than appears as such at the end, as a part seems to be converted to dextrin by the diastase in the yeast extract.

#### *Experiments with Taka-diastase.*

Taka-diastase, as is well known, very readily hydrolyses soluble starch. When the hydrolysis is allowed to approach completion, the final product has an optical factor corresponding with that of glucose.

#### *Experiment IV.*

A flask containing 100 c.c. of starch mucilage, 0.1 gram of taka diastase, and a few drops of toluene was put in a thermostat at 29°.

After 20 hours the optical factor was reduced to 0.985.

|   |        |   |   |                                     |   |        |
|---|--------|---|---|-------------------------------------|---|--------|
| „ | 7 days | „ | „ | „                                   | „ | 0.670. |
| „ | 15 „   | „ | „ | „                                   | „ | 0.545. |
| „ | 18 „   | „ | „ | not greater than<br>that of glucose |   | 0.525. |

On adding to a litre of starch mucilage at the ordinary temperature 0.4 gram of taka-diastase (a still smaller proportion of the ferment), the optical factor was reduced to 0.585 in 75 days.

Taka-diastase hydrolyses maltose, but its action is slower than the equivalent of dry yeast-extract.



*Experiment V.*

A flask containing 2.0 grams of maltose hydrate, 0.2 gram of taka-diastase made up with water to 50 c.c., with the addition of a few drops of toluene was put in a thermostat at 29° and examined after 4 days, when it was found that 80 per cent. of the maltose had been hydrolysed.

Taka-diastase also hydrolyses revertose (*vide* Exp. III).

In concentrated maltose solutions, taka-diastase, according to the polarimetric and copper estimations, apparently carries the hydrolysis farther than does yeast extract. The difference is, however, only apparent, and is due to other complicating factors; in the case of yeast-extract, there is a reversion of glucose to revertose, so that the quantity of maltose remaining at the end is much less than would appear from the measurements; in the case of taka-diastase, the formation of revertose is possibly proportionately slower, for it is not yet certain whether the ferment which produces revertose is identical with maltase, and further, another substance is formed of lower optical activity than revertose.

I am not at present in a position to give the analysis of the products formed by taka-diastase, but it is necessary to call attention to the fact that in the following experiments no inferences can be drawn as to the quantity of the synthetical bioses formed; the measurements represent quantitatively the sum of the changes in the several reactions, and prove that the action of taka-diastase is a reversible one.

*Experiment VI.*

Hydrolysis of maltose by taka-diastase in 40 per cent. sugar solutions containing 34 per cent. of glucose and 6 per cent. of maltose hydrate. The initial optical factor is 0.70, this being approximately the equilibrium factor when yeast-extract has acted on a 40 per cent. solution of either maltose or glucose.

Flask *A* contained 17 grams of glucose, 3 grams of maltose hydrate, 0.5 gram of taka-diastase, made up with water to 50 c.c. with the addition of toluene.

The contents of flask *B* were similar, but the ferments were destroyed by heat. Both flasks were placed in the thermostat at 29°.

Flask *A*, at the start, had an optical factor 0.695, and after 13 and 37 days the values of this factor had diminished to 0.585 and 0.580 respectively. Beyond this point, no further change was noticed, and no alteration was observed in flask *B*.

This shows the different optical factor which is reached in equilibrium when taka-diastase is used from that found with yeast-extract.

Approaching the equilibrium point from the other side, that is, starting with glucose, the reverse action with taka-diasase is shown thus:

### Experiment VII.

A flask, *A*, contained 150 grams of glucose, 2 grams of taka-diasase, with addition of water to 250 c.c. To the solution (sp. gr. 1.2245), a few drops of toluene were added.

A control flask, *B*, containing a similar mixture, was steamed and boiled, the ferment being thus almost completely destroyed. It was noted that in these highly concentrated solutions containing 60 per cent. of sugar, the ferment becomes more resistant to heat, the resistance appearing to increase with the concentration of the sugar on which the ferment acts.

Both flasks were placed in the thermostat at 29°.

At the start, *A*, optical factor 0.524; *B*, optical factor 0.524

After 4 days, *A*     "     "     0.549

"   8   "   *A*     "     "     0.556; *B*     "     "     0.525

"   22   "   *A*     "     "     0.559

"   30   "                    *B*     "     "     0.528

When a portion of the solution from flask *A* was diluted with water to 20 volumes and placed in the thermostat for 2 days, the optical factor diminished from 0.556 to 0.525, showing that the reversion was reversed.

The remainder of the fermented solution was heated for 2 hours at 100° with the result that the optical factor increased slightly from 0.560 to 0.565. A portion was then diluted to 5 times its volume and fermented with *S. Marxianus* in the manner previously described. A part also was fermented with *S. Ellipsoideus* I, and another part with *S. Cerevisia* Saaz.

| Variety of yeast.         | Duration of fermentation. | Optical factor before fermentation. | Optical factor after fermentation. | Residual optical activity. |
|---------------------------|---------------------------|-------------------------------------|------------------------------------|----------------------------|
| <i>S. Marxianus</i> ...   | 3 weeks                   | 0.56                                | 0.60                               | 3.54°                      |
| 7½ "                      |                           | 0.56                                | 2.01                               | 1.21                       |
| <i>S. Ellipsoideus</i> I. | 3 "                       | 0.56                                | 1.71                               | 0.59                       |
| <i>S. Cerev. Saaz</i> ... | 3 "                       | 0.56                                | 1.56                               | 0.84                       |

The fermentation with the last-named yeast was not complete, but it was shown that a portion of the product not fermented by *S. Marxianus* was fermented by *S. Ellipsoideus*, also that the synthetical products were partly fermented by *S. Cerev. Saaz*.

The contents of the control flask, when diluted and fermented with *S. Marxianus*, left only a small, unfermented residue, this result corresponding with a very slight synthetical change.

### *Examination of the Products.*

The synthetical products from about 111 grams of glucose were, after fermentation with *S. Marxianus*, obtained in concentrated solution by evaporating the fermented solution in the manner already described. On pouring the syrup into boiling concentrated ethyl alcohol, there was a voluminous precipitate, which was not entirely soluble in water. The aqueous extract of this precipitate had an optical factor 1.8, its reducing power on hydrolysis with dilute hydrochloric acid being nearly trebled, with only a small decrease (about 14 per cent.) in the optical activity.

The hot alcoholic filtrate from the above precipitate deposited on cooling a syrup which increased in quantity when the mixture was left in a desiccator over lime. The semi-solid product, when separated from the supernatant mother liquor, extracted with absolute alcohol, and left in the desiccator, yielded a hygroscopic, crystalline substance, weighing about 5 grams and having an optical factor of 2.05 ( $[\alpha]_D$  = about  $80^\circ$ ,  $R$  = about 40). By extraction with boiling 80 per cent. ethyl alcohol, this substance was divided into two fractions, the portion which dissolved in the hot alcohol and separated on cooling having an optical factor of 2.19, whilst the value of this constant for the insoluble residue was 1.90. The mother liquor from the soluble fraction had an optical factor 1.82. There were thus two or three optically active substances present, beside a small proportion of inorganic salts. The synthetical product of the taka-diastrase reaction yields an osazone resembling in appearance that obtained from the mixed bioses formed by yeast extract. It is probably a mixture and was not further investigated.

The above reversed and reversible change was observed with 60 per cent. glucose solutions, but it can be readily followed with a good polarimeter in 40 per cent. solutions.

### *Experiment VIII.*

A flask containing 40 grams of glucose, 1 gram of taka-diastrase, diluted with water to 100 c.c. with the addition of toluene, the solution having a sp. gr. 1.153, was placed in the thermostat at  $29^\circ$ , and from time to time quantities of 1 c.c. were withdrawn and diluted to 20 c.c. with distilled water, immediately examined with the polarimeter, then allowed to stand for 24 or 48 hours at the room temperature for hydrolysis to take place (since the synthetical



action is reversed on dilution), and again examined. The portions removed for analysis were weighed and corrections made for the small variations in the 1 c.c. withdrawn, so that the successive readings are comparable.

= At the start,  $a_D = 2.06^\circ$

After 8 days,  $a_D = 2.13$ , re-examined after 24 hours,  $2.07^\circ$

„ 23 „  $a_D = 2.16$ , „ „ 48 „  $2.08$

„ 55 „  $a_D = 2.18$ , „ „ 48 „  $2.08$

The contents of a control flask which had been boiled showed no change when left in the thermostat. The synthetical products due to taka-diastase are also hydrolysed by yeast-extract, but the hydrolysis is possibly incomplete, or a portion of these products is hydrolysed only slowly. The yeast extract used in this experiment had been prepared a few weeks and was then rather feeble. The synthetical products of Experiment VII were used, diluted to 20 volumes. The sugar concentration of the solution was thus 3 per cent. and the concentration of yeast-extract was equivalent to 0.15 per cent. of the dried extract.

At the start, optical factor was 0.56 and 0.535 after 10 days. The control flask examined after 10 days gave 0.56.

### *Experiments with Pancreatic Ferments.*

In these experiments, I used an extract of pig's pancreas, prepared with dilute alcohol, for which I am indebted to Mr. F. Baden Benger. The preparation, which was especially active in diastase, also contained some trypsin and maltase; 5 c.c. of this solution acting on a litre of 5 per cent. starch solution at a temperature of  $30^\circ$  reduced the optical factor to 4.62 in 5 days. In order to test whether, in the hydrolysis of starch by pancreatic diastase, the equilibrium point varies with the concentration, the following experiment was performed:

#### *Experiment IX.*

Flask A, containing 100 c.c. of the above solution (optical factor, 4.6), 2 c.c. more ferment solution, diluted with water to 200 c.c.

Flask B, 200 c.c. of the above solution (optical factor, 4.6) with 2 c.c. more ferment solution.

Flask C, 100 c.c. of the above solution (optical factor, 4.6).

The three flasks were placed in the thermostat at  $30^\circ$  and re-examined after 4 weeks. The optical factors of A, B, and C were found to be 2.01, 3.215, and 3.54 respectively. The change was much more rapid in A, where the concentration of the products of

starch hydrolysis was 2.5 per cent., than in *B*, where it was 5 per cent., although the concentration of the ferment was approximately the same in each, but slightly greater in *B*.

It has been found possible to show that the pancreatic ferments have a reversible synthetical action on glucose; the reaction was complicated by the formation of one substance at least of lower optical activity than glucose, and corrections were required for the lævotation of the ferment solution itself. Nevertheless, there is a small increase in optical factor in concentrated glucose solutions, and it falls again on dilution of the solution if the ferments are not destroyed.

The sugar concentration in the experiments was 60, and the procedure was as described in the experiments with taka-diastase. The optical factors are corrected for the lævotation of the ferment solution, this means that about 0.005 has been added to the values found at both the beginning and end of the experiments.

#### *Experiment X.*

Optical factor at the start, 0.524 (corrected).

„ „ after 17 days, 0.538 „

There was no change in the control.

On diluting 1 c.c. to 20 c.c., the optical factor diminished to 0.528 in 24 hours.

The rest of the solution was boiled, diluted to 6 volumes with tap-water, and fermented for 20 days with *S. Marxianus*, whereby the optical factor was raised to 1.22 (uncorrected).

#### *Experiment XI.*

This was similar to the last experiment, but on a somewhat larger scale, about 300 grams of glucose being employed in 62 per cent. solution.

At the start, and after 19 and 48 days, the corrected optical factors were 0.526, 0.5375, and 0.539 respectively.

There was no appreciable change in the control.

After the solution was boiled and allowed to cool, glucose began to crystallise out, about half being separated in this way. The mother-liquor, containing the remainder of the unchanged glucose together with synthetical products, was diluted with tap-water and fermented by *S. Marxianus*, the control solution being similarly treated. The solutions then gave the following measurements.

After fermentation,  $\alpha_D = 0.44^\circ$  (uncorrected),  $\rho$  = the equivalent of a 0.266 per cent. solution of glucose. Optical factor = 0.825 (uncorrected).

Control  $a_D = 0.044^{\circ}$  (uncorrected),  $\rho$  = the equivalent of a 0.15 per cent. solution of glucose. Optical factor = 0.145 (uncorrected).

The difference in residual opticity between the experimental solution and the control is well marked. The synthetical change in these experiments was small, but it was of the same character as the larger one observed with taka-diastase and as the still larger one with yeast extract, and is sufficient to establish the fact that enzymes of animal origin, which act on carbohydrates, as well as those obtained from plants, do so in a reversible manner.

### Summary.

(1) It is shown that the synthetical action of a maltase-containing yeast-extract on glucose results in the formation of two isomeric bioses—one, not hitherto described, which is now called *revertose*; the other, although not isolated, is, according to the evidence obtained, in all probability maltose. A small formation of dextrin is attributed to the diastase in the yeast-extract.

(2) It is shown, further, that both taka-diastase and the pancreatic ferments have a reversible synthetical action on glucose.

Since I published my first paper on this subject, there have appeared from time to time, besides some small contributions by myself, observations by others of a similar nature, further extending the list of ferments for which a reversible action has been noted. Kastle and Loevenhart found that lipase had a reversible action on ethyl butyrate (*Amer. Chem. J.*, 1900, 24, 491). Hanriot also independently observed the reversible action of lipase (*Compt. rend.*, 1901, 132, 212). Wroblewski was able to detect a reversible action with invertase, but I have not had the opportunity of seeing his original paper (*Bull. Acad. Sci. Cracow*, 1901, 94—95). O. Emmerling has recorded another synthesis with yeast-extract, namely, that of amygdalin from glucose and mandelonitrile glucoside (*Ber.*, 1901, 34, 3810). Recently, Emil Fischer and E. F. Armstrong have noted the reversible action of kephir-lactase on a new biose, *isolactose*, which yields glucose and galactose on hydrolysis (*Ber.*, 1902, 35, 3146), and, more recently still, Acree and Hinkins have found the hydrolysis of triacetyl-glucose by pancreatin to be reversible (*Amer. Chem. J.*, 1902, 28, 370—376). These observations, together with my own more recent results, make it increasingly more probable that the view I put forward in 1898 is a correct one—namely, that all ferment actions are reversible, and appear to warrant the adoption of such a view as a sound working hypothesis.



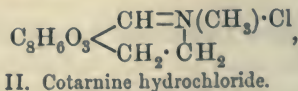
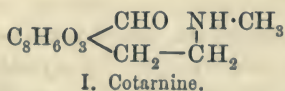
The cost of the material in this research was partly covered by a grant from the Government Grants Committee of the Royal Society, to whom my thanks are due. I am much indebted to the Directors of the Davy-Faraday Research Laboratory of the Royal Institution for the use of laboratories, instruments, and many reagents, and to Dr. A. Scott for many acts of kindness. I wish also to acknowledge the considerable help received from a tenure of the George Henry Lewes Studentship in Physiology during the period in which most of the work was performed.

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#### LXIV.—*The Constitution of Cotarnine.*

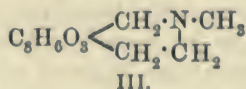
By JAMES J. DOBBIE, M.A., D.Sc., ALEXANDER LAUDER, B.Sc., and  
CHARLES K. TINKLER.

ROSER (*Annalen*, 1888, 249, 156, 168; 1889, 254, 334, 359) assigned to cotarnine and its hydrochloride the following formulæ:



assuming that in the formation of the salt from the base a molecule of water is eliminated and a pyridine ring formed which is not present in cotarnine itself. By acting on cotarnine with methyl iodide, he found that two methyl groups were taken up and hence inferred that the base must be secondary, and not tertiary as formerly supposed. He considered that the presence of an aldehyde group both in cotarnine and cotarnmethine methochloride was proved by the formation of a crystalline compound with hydroxylamine hydrochloride, but admitted that the aldehyde formula failed to explain the following facts:

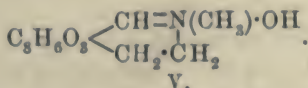
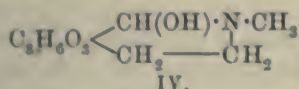
- (1) the relationship of the tarconine derivatives to cotarnine;
- (2) the precipitation from its salts of cotarnine in the aldehyde form;
- (3) the oxidation of hydrocotarnine



to cotarnine.

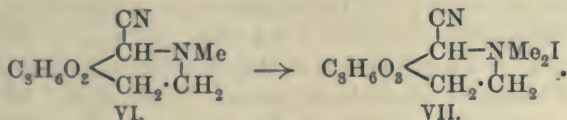
Decker (*J. pr. Chem.*, 1893, 47, 222), in drawing attention to the improbability of an aldehyde residue and a secondary amine group co-existing in the same molecule, indicated other difficulties

in the way of the acceptance of Roser's formula, and proposed to substitute for it the following formula, IV, in which cotarnine is represented as a carbinol base :



Hantzsch and Kalb (*Ber.*, 1899, 32, 3109), who investigated the conductivity of cotarnine solutions, suggested in explanation of the anomalous results which they obtained that such solutions may consist of a mixture in equilibrium of two or possibly three forms of cotarnine, namely, the ammonium base V, corresponding with the cotarnine salts II, the carbinol form IV proposed by Decker, and Roser's open chain aldehyde form I.

The sparingly soluble cyanide of low electrical conductivity obtained by Freund and Kalb from cotarnine hydrochloride and potassium cyanide is similar in every respect to the cyanides of the acridinium bases, and accordingly these investigators concluded that this derivative was not a true salt of cotarnine comparable with the hydrochloride II. This view was confirmed by Freund (*Ber.*, 1900, 33, 380), who obtained a methiodide from the cyanide and showed that this result is most readily explained by assuming that the latter compound is a carbinol derivative :



From the foregoing summary, it appears that three formulæ have been proposed for cotarnine and cotarnine derivatives, namely, Roser's aldehyde formula, I; Decker's carbinol formula, IV; and the ammonium formula, V. There is, however, no agreement as to which of these formulæ should be assigned to solid cotarnine, and, according to Hantzsch (*Ber.*, 1900, 33, 3685), the existing data are insufficient to decide this point. We believe, however, that the necessary evidence for answering this question definitely and for determining in which form cotarnine exists in solution in a particular solvent is afforded by a study of the absorption spectra of these substances.

Whilst solutions of cotarnine in ether or chloroform are, like the solid base, quite colourless, its solutions in water or alcohol are yellow, a change taking place as soon as the alkaloid comes into contact with either of the last-mentioned solvents. Since there is no reason to suppose that either ether or chloroform has any action on cotarnine, the absorption spectra of the solutions in these solvents may be

regarded as the true absorption spectra of this substance. These spectra agree closely with those of hydrocotarnine, a substance which is generally considered to have the constitution represented by III (Plate I).

This agreement is altogether inexplicable if the constitution represented by Roser's formula is accepted for cotarnine, but it is at once explained by the adoption of the carbinol formula, which represents cotarnine as differing from hydrocotarnine only in the substitution of a hydroxyl group for an atom of hydrogen. Moreover, the spectra of cotarnine in ether or chloroform are practically identical with those of the cyanide which Hantzsch and Kalb represent as being a derivative of the carbinol form (Plate III, Figs. 1 and 9).

A very dilute aqueous or alcoholic solution of cotarnine, on the other hand, gives spectra practically identical with those of cotarnine hydrochloride (Plate II), which are widely different in character from the spectra of cotarnine in ether. The same spectra are also given by a solution of cotarnine hydrochloride from which the chlorine has been removed by means of silver oxide.

It thus appears that cotarnine and all its derivatives, which we have so far examined spectroscopically, conform to one or other of these two forms of spectra.\*

(1) Spectra showing a large amount of general absorption and having two well-marked absorption bands, one of which is close to the visible region of the spectrum;  $\lambda$  3278 indicates approximately the middle of one band, and  $\lambda$  2500 the middle of the other (Plate II †). Cotarnine in dilute aqueous or alcoholic solution, the cotarnine salts, and the hydrochloride of cotarnine oxime have spectra of this type. All the substances of this class are yellow, and are generally represented by the formulæ II and V.

(2) Spectra showing less general absorption than the former, and having one band which does not coincide in position with either of the bands in the former spectra;  $\lambda$  2857 indicates approximately the position of this band (Plate I). Solutions of cotarnine in ether or chloroform, hydrocotarnine and its salts, ethoxyhydrocotarnine, and cyanohydrocotarnine have spectra of the second type; these substances are colourless, and can all be easily represented by means of the carbinol formula. The spectra of the oxime also agree closely with the spectra of this group, but in the absence of information as to the relationship generally existing between the spectra of oximes and those of the substances from which they are derived, we do not wish to lay stress on this result.

\* The choice of derivatives is necessarily limited to those which do not contain groups exercising a marked influence on the character of the spectra.

† Only the first of these bands is shown in the part of the photograph reproduced, the second band alone appearing in the spectra of more dilute solutions.



Our attention was first directed to the problem of the constitution of cotarnine by the remarkable action of alcohol on this substance. In general, no sudden change is produced in the character of the spectra of a substance by mere dilution; as the concentration diminishes, the extent to which the spectrum is transmitted gradually increases, and the absorption bands disappear. In the case of the alcoholic cotarnine solution, however, it was noticed that on increasing the dilution, the extent to which the spectrum was transmitted was diminished, and the position of the absorption bands altered.

This peculiarity in the behaviour of cotarnine could only be accounted for by assuming that the action of the alcohol brought about a constitutional change. It is remarkable that until quite recently little attention has been paid to the action of alcohol on cotarnine, although it has been known ever since the substance was discovered that its solution in alcohol has an intense yellow colour. Cotarnine, when treated with methyl iodide in presence of alcohol, yields the methiodide of ethoxyhydrocotarnine (Roser, *loc. cit.*), and quite recently Freund and Bamberg (*Ber.*, 1902, 35, 1739) have prepared ethoxyhydrocotarnine by dissolving cotarnine in absolute alcohol and evaporating the solution under diminished pressure. They consider that certain of the reactions of this substance are best explained by regarding it as a derivative of the carbinol form, VIII, whilst others suggest the ammonium configuration, IX:



The fact that this compound is colourless points to the former formula as being more appropriate, and this is supported by the examination of the spectra of the substance in ethereal solution, which are the same as those of cotarnine in ether.

The action of the alcohol, however, does not end with the formation of ethoxyhydrocotarnine. The alcoholic solution of this substance rapidly becomes coloured, and then gives absorption spectra differing widely from the spectra of its colourless ethereal solution and approaching more and more closely, according to the conditions, to the spectra of cotarnine hydrochloride. When, therefore, solid cotarnine is treated with successively larger quantities of alcohol, or when successively larger quantities of alcohol are added to the ethereal solution of cotarnine, the base changes from the carbinol to the ammonium form, and the absorption spectra are seen to pass gradually from those characteristic of the one form to those characteristic of the other (Plate III, Figs. 1—8). The change can be traced through all its phases by carefully regulating the

conditions, and it is even possible to estimate, at least approximately, the extent to which the change has proceeded by comparing the spectra of the solutions with those of a series of solutions containing mixtures in definite proportions of cotarnine hydrochloride and cyanohydrocotarnine (Plate III, Figs. 9—16; Table I, p. 604). Whether the final product of decomposition is an ethoxy-compound of the form represented by IX, or merely the ammonium base V, it is impossible to decide with certainty, since the spectra of both substances would be the same, the difference between the compounds consisting merely in the substitution of  $C_2H_5$  for H.

The action of methyl alcohol on cotarnine is even more marked than that of ethyl alcohol. By dissolving 1 milligram-mol. of cotarnine in 500 c.c. of ethyl alcohol, 10 per cent. is converted into the ammonium base form, whilst the proportion changed by dissolving the same weight in methyl alcohol is between 20 and 30 per cent.

The action of alcohol is accelerated by heating. Time also has an important influence on the change, the spectra of an alcoholic solution which has been kept for some time indicating a closer approximation to the spectra of cotarnine hydrochloride than those of the same solution when freshly prepared.

The final result of the action of alcohols on cotarnine is the same as that of hydrochloric acid, but whilst the action of the acid brings about the transformation in an inappreciably short space of time, the change under the influence of alcohol proceeds slowly unless assisted either by heating or by the presence of a large mass of the solvent.

Alkalis tend to change the ammonium form of cotarnine into the carbinol form, their action being the reverse of that of acids, water, or alcohols.

When a solution of cotarnine hydrochloride is decomposed with sodium hydroxide, the base is obtained at once in the carbinol form, the transformation taking place with extreme rapidity, just like the inverse change induced by acids. If, however, an aqueous solution of cotarnine is treated with successively larger quantities of sodium hydroxide, the change from the ammonium base to the carbinol form may be traced through all its phases (Plate III, Figs. 17—24), and as in the case of the opposite change under the influence of alcohol, the extent to which the change has proceeded under any given set of conditions may be approximately estimated (see Table II, p. 605).

Potassium and barium hydroxides act similarly, equivalent quantities of these bases producing practically the same effect as sodium hydroxide. The amount of change produced by an equivalent amount of ammonia is, on the other hand, very much smaller. Heating appears to retard the action of the alkalis.

So far we have failed to find any evidence of the existence of more



than two forms of cotarnine in solution. We have been able by means of mixtures of cyanohydrocotarnine (carbinol form) and cotarnine hydrochloride (ammonium form) to reproduce all the appearances shown by the photographs of solutions of cotarnine changing under the influence of alcohol or sodium hydroxide.

We have failed to find any justification for the view (Freund, *Ber.*, 1900, 33, 380) that cyanohydrocotarnine consists of a mixture in equilibrium of two forms. No doubt this substance readily undergoes change like the other cotarnine derivatives, but the fact that its spectra are almost identical with those of an ethereal solution of cotarnine shows that it cannot be mixed to any appreciable extent with a derivative of the ammonium form.

The foregoing observations on the conditions under which cotarnine undergoes isomeric change explain to a large extent the anomalous results obtained by Hantzsch and Kalb (*Ber.*, 1899, 32, 3109) in their experiments on the conductivity of cotarnine solutions. The increase in the value of  $K$ , observed when the temperature of the aqueous solution is raised from  $0^{\circ}$  to  $25^{\circ}$ , is no doubt due to the influence of heat in promoting the conversion of the carbinol into the ammonium form of the base. The system, cotarnine hydrochloride—NaOH, at once gives a constant conductivity because, as the spectra show, the change from the ammonium base to the carbinol form is practically complete in an inappreciably short space of time. The smaller conductivity of the solution obtained in this way as compared with that of an aqueous solution of cotarnine is obviously due to the circumstance that the former contains the carbinol form, whilst the latter, if sufficiently dilute, contains chiefly the ammonium form. Lastly, the solution obtained from cotarnine hydrochloride by removing the chlorine with silver oxide gives a higher value for  $K$  than the aqueous solution, because, on the removal of the chlorine, practically the whole of the cotarnine is at once obtained in the ammonium form, whereas when cotarnine is dissolved in water the transformation requires for completion a high degree of dilution.

The experiments described in this paper have been carried out primarily with the object of throwing light on the constitution of cotarnine and its derivatives. It is obvious, however, that they afford a basis for interesting observations on the rate of transformation and on the conditions which influence isomeric change, and also that they may possibly afford a means of comparing the influence of the various acids and alkalis in promoting or hindering such changes. We are now engaged on a series of accurate experiments in this connection.

Hydrastinine, which seems to behave in the same way as cotarnine



under the influence of alcohol and other reagents, is also under investigation.

### EXPERIMENTAL.

The cotarnine employed, which was prepared from narcotine by the method given by Anderson (*Annalen*, 1853, 86, 187) and purified by Beckett and Wright's method (*Trans.*, 1875, 28, 576), melted at 132—133°. The hydrocotarnine was prepared by the reduction of cotarnine, and melted at 55° (Beckett and Wright, *loc. cit.*). The cyanide (m. p. 94°) was obtained by the action of potassium cyanide on the hydrochloride (*Ber.*, 1899, 32, 3130); the ethoxy-derivative, which was prepared by dissolving cotarnine in the least possible quantity of absolute alcohol, and rapidly evaporating off the alcohol under diminished pressure, crystallised in colourless crystals melting at 83° and decomposing at 125° (Freund, *Ber.*, 1902, 35, 1739).

The hydrochloride of cotarnine oxime, prepared by the action of a slight excess of hydroxylamine hydrochloride on an alcoholic solution of cotarnine, is a yellow, crystalline substance, which, on treatment with sodium carbonate, yields the oxime, the latter being a colourless, crystalline compound melting at 165° (*Annalen*, 1889, 254, 334).

TABLE I.

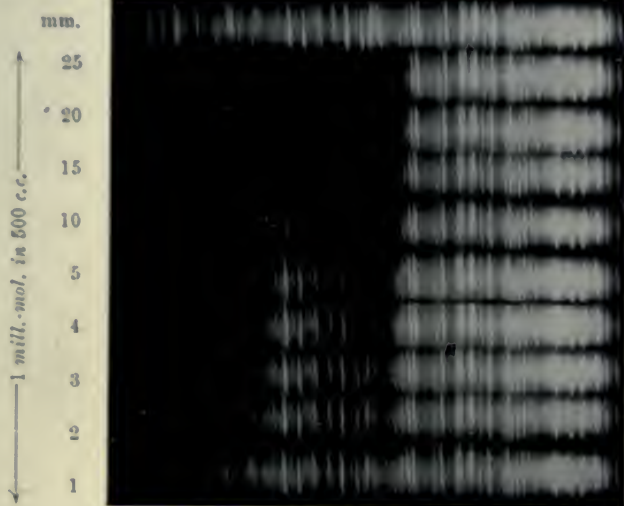
*Effect of the Gradual Addition of Methyl Alcohol to an Ethereal Solution of Cotarnine at the Ordinary Temperature.*

| Percentage of methyl alcohol. | Carbinol form. | Ammonium base form. | Plate III. |
|-------------------------------|----------------|---------------------|------------|
| 0 per cent.                   | 100 per cent.  | —                   | 1          |
| 25    "                       | 97·5    "      | 2·5 per cent.       | 2          |
| 40    "                       | 92·5    "      | 7·5    "            | 3          |
| 50    "                       | 85    "        | 15    "             | 4          |
| 100   "                       | 75    "        | 25    "             | 5          |

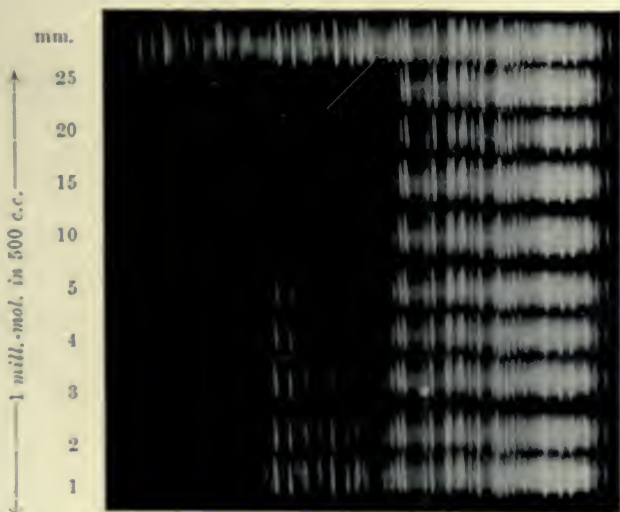
The conversion into the ammonium base form is practically completed either by warming the alcoholic solution or by allowing it to remain for a sufficient length of time (see Plate III, Figs. 6 and 7).

The numbers representing the amount of change in the foregoing table are only approximate. They have been obtained by comparison with photographs of the spectra of mixtures in known proportions of cyanohydrocotarnine (carbinol form) and cotarnine hydrochloride (ammonium form). Some of the mixtures were checked against mix-

PLATE I.



*Hydrocotarnine.*



*Colarnine (in ether).*

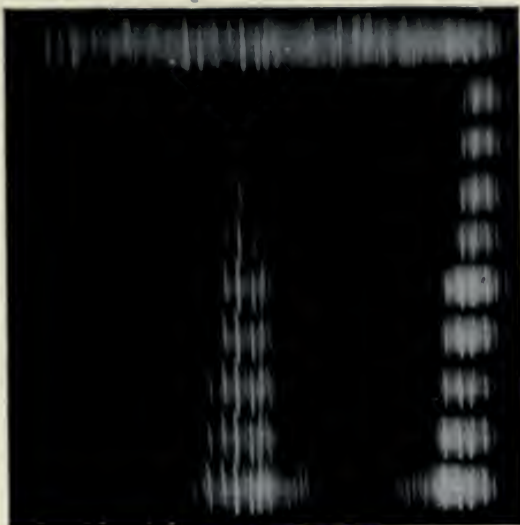




PLATE II.

mm.  
25  
20  
15  
10  
5  
4  
3  
2  
1

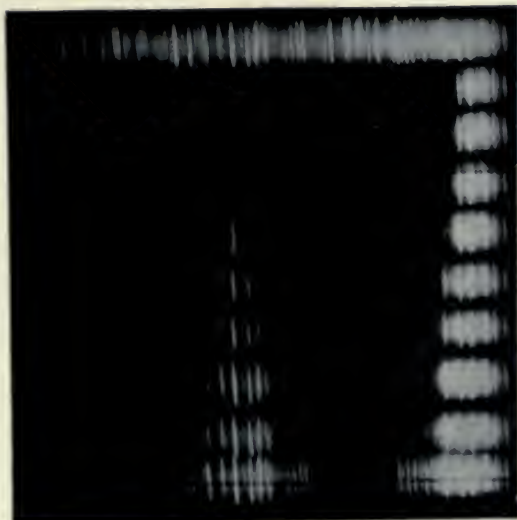
1 mill.-mol. in 500 c.c.



*Cotarnine hydrochloride.*

mm.  
25  
20  
15  
10  
5  
4  
3  
2  
1

1 mill.-mol. in 500 c.c.



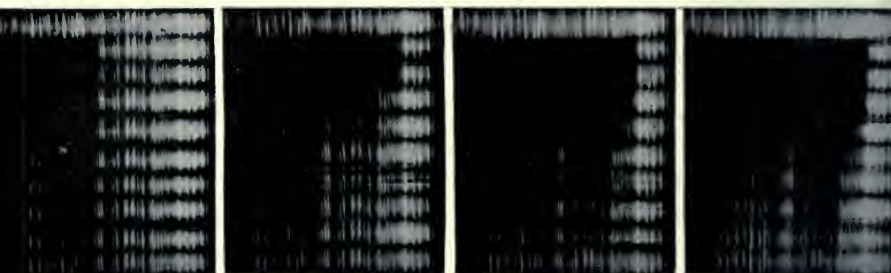
*Cotarnine (in water).*







## Effect of the gradual addition of methyl



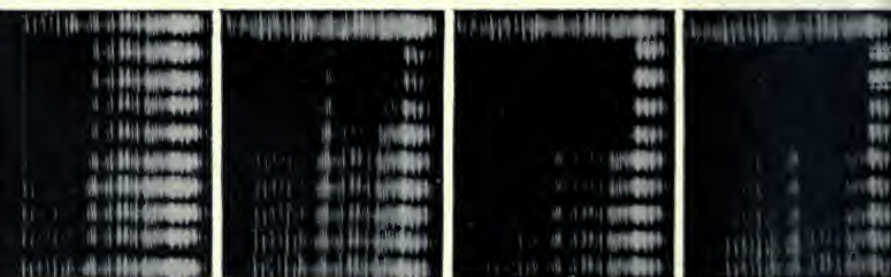
1  
Cotarnine in  
ether;

2  
Cotarnine in  
ether..... 75 % }  
methyl alcohol 25 % }

3  
Cotarnine in  
ether..... 60 % }  
methyl alcohol 40 % }

4  
Cotarnine in  
ether..... 50 % }  
methyl alcohol 50 % }

Absorption spectra of mixtures in various proportions of cyanohydrocotarnine



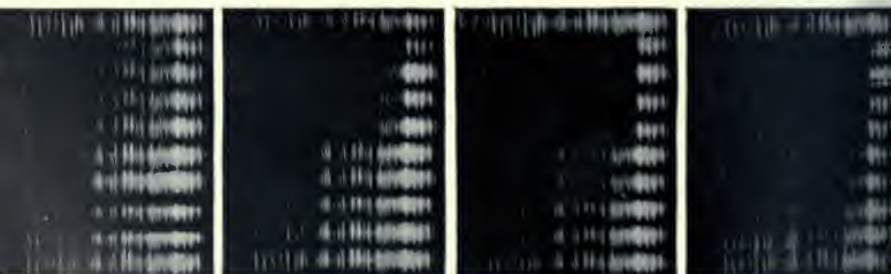
9  
Cyanohydrocotarnine.

10  
Mixture of  
cyanide ..... 97.5 % }  
hydrochloride.. 2.5 % }

11  
Mixture of  
cyanide ..... 95 % }  
hydrochloride 5 % }

12  
Mixture of  
cyanide ..... 90 % }  
hydrochloride... 10 % }

## Effect of the gradual addition of sodium



17  
Cotarnine in 2N  
sodium hydroxide.

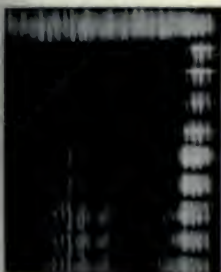
18  
Cotarnine in  
N/2 NaOH.

19  
Cotarnine in  
N/5 NaOH.

20  
Cotarnine in  
N/10 NaOH.

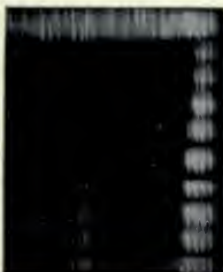
### III.

alcohol to an ethereal solution of cotarnine.



5

Cotarnine in methyl alcohol.



6

Cotarnine in methyl alcohol heated for 10 mins. at 40°.



7

Cotarnine in methyl alcohol heated for 30 mins. at 40°



8

Cotarnine hydrochloride.

(carbinol form) and cotarnine hydrochloride (ammonium base form).



13

Mixture of  
cyanide ..... 70 % }  
hydrochloride. 30 % }



14

Mixture of  
cyanide ..... 40 % }  
hydrochloride.. 60 % }



15

Mixture of  
cyanide ..... 20 % }  
hydrochloride.. 80 % }



16

Cotarnine hydrochloride.

hydroxide to an aqueous solution of cotarnine.



21

Cotarnine in  
N/50 NaOH.



22

Cotarnine in  
N/100 NaOH.



23

Cotarnine in  
N/500 NaOH.



24

Cotarnine hydrochloride.





TABLE II.

*Effect of Sodium Hydroxide on an Aqueous Solution of Cotarnine at the Ordinary Temperature.*

| Strength of sodium hydroxide. | Carbinol form. | Ammonium base form. | Plate III, fig. |
|-------------------------------|----------------|---------------------|-----------------|
| N/500 NaHO                    | 20 per cent.   | 80    "             | 23              |
| N/100    "                    | 40    "        | 60    "             | 22              |
| N/50     "                    | 70    "        | 30    "             | 21              |
| N/10    "                     | 90    "        | 10    "             | 20              |
| N/5     "                     | 95    "        | 5     "             | 19              |
| N/2     "                     | 97.5   "       | 2.5   "             | 18              |
| 2N     "                      | 100    "       | —                   | 17              |

tures containing hydrocotarnine in place of the cyanide. In every case the results were identical.

The method adopted in photographing the spectra has already been described in former papers.

The top line in each photograph shows the spectrum of the alloy of cadmium, tin, and lead. The photographs in plate III are directly comparable with those in plates I and II, the same strength of solution and layers of the same thickness being employed in each case.

It may be mentioned that the photographs in plate III are only a selection from the series taken.

We again desire to express our cordial thanks to Professor W. N. Hartley for kindly lending us the apparatus with which the experiments were carried out.

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BANGOR.

## LXV.—*On the Relation between the Absorption Spectra and the Chemical Structure of Corydaline, Berberine, and other Alkaloids.*

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER, B.Sc.

IN a paper read before the Society in December, 1901 (Trans., 1902, 81, 145), we communicated the results of our investigation on the constitution of corydaline, and showed that this alkaloid is closely related to berberine. We have since been engaged in the spectroscopic

examination of these two alkaloids and their decomposition products, and we now propose to lay the results of this supplementary investigation before the Society, with the object mainly of showing that the spectroscopic method might, with advantage, be generally employed in such researches.

In a paper communicated to the Royal Society eighteen years ago by Professor Hartley (*Phil. Trans.*, 1885, Part II, 471), it is shown that the principal alkaloids give highly characteristic absorption spectra which can be used for their identification and for ascertaining their purity. It is further shown that alkaloids closely related to one another, like quinine and quinidine, cinchonine and cinchonidine, morphine and codeine, give very similar spectra. At the time at which this paper was published, however, little progress had been made with the investigation of the alkaloids, and it was not possible, therefore, to trace any close connection between their structure and their spectra.

The constitution of the principal members of the group of alkaloids to which corydaline and berberine belong, namely, papaverine, hydrastrine, narcotine, and narceine, has now been definitely determined, and the examination of this group furnishes a good basis for the study of the relationship between the absorption spectra and the constitution of the alkaloids.

Since papaverine is, in some respects, more simply constituted than the other members of the group, it will be convenient to consider each of the others with reference to it. According to Goldschmiedt, the structure of papaverine is represented by the following formula :

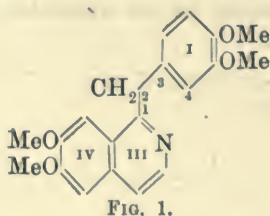


FIG. 1.

A graphic representation of the absorption spectra of papaverine is given in Fig. 8, p. 616. The spectra show two absorption bands, the first lying between  $1/\lambda$  2998 ( $\lambda=3335$ ) and  $1/\lambda$  3295 ( $\lambda=3035$ ), and the second between  $1/\lambda$  3956 ( $\lambda=2528$ ) and  $1/\lambda$  4555 ( $\lambda=2195$ ).

Hydrastrine differs structurally from papaverine in the following particulars : (i) The isoquinoline nucleus is partially reduced. (ii) The two methoxyl radicles of the isoquinoline nucleus are replaced by a dioxymethylene group. (iii) A methyl group is attached to the nitrogen atom. (iv) A carbonyl group is attached to the carbon atom (4), and through the medium of an oxygen atom is also linked to carbon atom

(2), which has only one atom of hydrogen attached to it. From this comparison, it is obvious that the two substances differ considerably in their constitution. On comparing the curve of the absorption spectra of hydrastine with that of papaverine (Figs. 10 and 8, pp. 617 and 616), it will be seen that there is a correspondingly wide difference between them; hydrastine exhibits slightly less general absorption than papaverine, and shows only one absorption band which is wider and much more persistent than either of the absorption bands of papaverine. Narcotine only differs from hydrastine in containing an additional methoxyl group attached to ring IV, and the two alkaloids give practically identical absorption spectra (Figs. 11 and 10, p. 617). Assuming the constitution of corydaline, as determined by us, to be correct, it is represented by the second of the following formulæ:

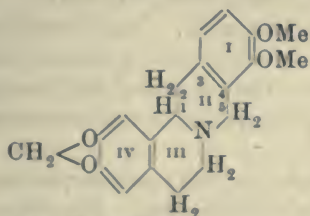


FIG. 2.—Tetrahydroberberine.

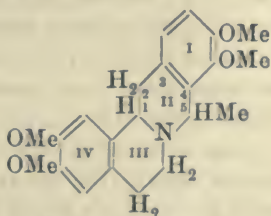


FIG. 3.—Corydaline.

On comparing this formula with that of papaverine, the differences will be seen to consist in the partial reduction of the isoquinoline nucleus and in the presence of carbon atom (5), which, with its associated methyl group, is linked on the one hand to carbon atom (4), and on the other to the nitrogen atom, thus forming a fourth closed chain in the molecule. Here, again, the difference between the absorption spectra and those of papaverine is very marked. The amount of general absorption is less, and there is only one absorption band, which is, however, better defined and more persistent than the papaverine bands (Figs. 8 and 12, pp. 616 and 618).

In discussing the relations between corydaline and berberine, it is to be remembered that corydaline corresponds to tetrahydroberberine, and berberine to dehydrocorydaline. The constitutional connection between corydaline and tetrahydroberberine is undoubtedly very close (Trans., 1902, 81, 145), as a comparison of the formulæ (Figs. 2 and 3, above) will show, and between the spectra of the two substances there is also a very close relation (Figs. 12 and 13, p. 618), the only difference being that the general absorption of tetrahydroberberine is slightly greater than that of corydaline.

When papaverine is reduced to tetrahydropapaverine, it is brought structurally very near to corydaline. A comparison of the formulæ of the two substances shows that the former substance differs from the

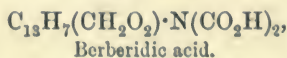
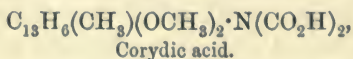


latter in the absence of carbon atom (5) of ring II with its associated hydrogen atom and methyl group. The spectra of the two compounds are almost identical (Figs. 9 and 12, pp. 616 and 618). Viewing corydaline as derived from tetrahydropapaverine by the addition of  $\text{CH}_2$  forming a fourth closed chain in the molecule, it might have been anticipated that the difference between the absorption spectra of the two substances would be greater than is found to be the case. It should be noted, however, that ring II in corydaline is a reduced ring, and would not therefore exert the same influence on the absorption spectra as the formation of a pyridine ring. It might be expected to produce an effect comparable with that produced by the substitution of a dioxymethylene for two methoxyl groups, which, we shall show later, is slight in compounds of high molecular weight (Hartley, Trans., 1885, 47, 691; Hartley and Dobbie, Trans., 1900, 77, 846).

Narceine is the extreme member of this group. It has two benzene nuclei, but no pyridine ring, and in other particulars differs considerably in constitution from papaverine. The absence of any absorption band differentiates the spectra widely from those of the other members of the group (Fig. 29, p. 609).

We have shown (Dobbie and Lauder, *loc. cit.*) that corydaline and berberine give rise to a parallel series of derivatives. The absorption spectra of the corresponding derivatives are related to one another in the same way as the spectra of the parent substances. When corydaline is acted on with mild oxidising agents, four atoms of hydrogen are removed, and a yellow substance is obtained, which stands in the same relation to corydaline as berberine to tetrahydroberberine (Trans., 1902, 81, 145).

Oxidation with dilute nitric acid converts corydaline and berberine respectively into the dibasic corydic and berberidic acids:



whilst oxidation with permanganate gives rise, amongst other products, to corydaldine in the former case, and to  $\omega$ -aminoethylpiperonylcarboxylic anhydride in the latter. The corresponding derivatives differ structurally from one another in the same way as corydaline and tetrahydroberberine, excepting that, in the case of corydaldine and  $\omega$ -aminoethylpiperonylcarboxylic anhydride, ring II having disappeared, the difference between the two compounds is confined to the replacement of the two methoxyl groups of the former by dioxymethylene in the latter. The spectra of the corresponding derivatives (Figs. 16 and 17, and 20 and 21, pp. 620 and 622) exhibit the same close relationship as those of the

alkaloids themselves. The general absorption of the berberine derivatives is, however, always slightly greater than that of the corresponding corydaline derivatives. This is probably due to the influence of the dioxymethylene group, and the correctness of this inference is supported by the fact that piperonylic acid,  $C_6H_5(CH_2O)_2 \cdot CO_2H$ , shows slightly greater general absorption than veratric acid,  $C_6H_5(OCH_3)_2 \cdot CO_2H$  (Figs. 18 and 19, p. 621).

Whilst the spectra of corydaline and  $\omega$ -aminoethylpiperonylcarb-

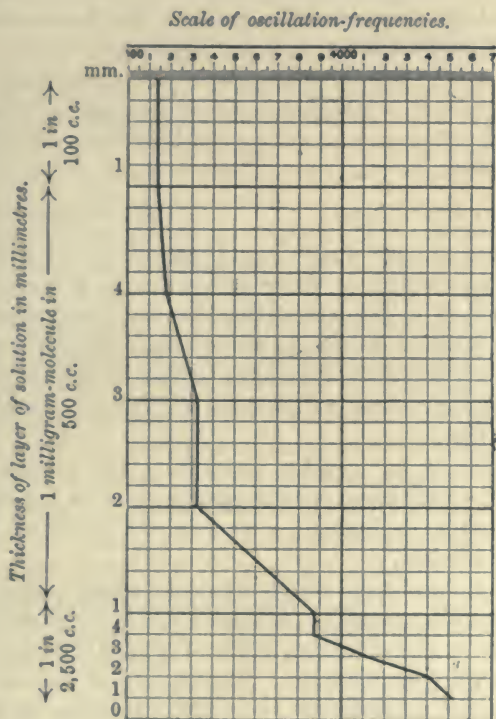


FIG. 29.—Narceine,  
 $C_{23}H_{27}O_8N + 3H_2O$ .  
 (In alcoholic solution.)

oxylic anhydride approach one another closely, they differ widely from those of cotarnine and hydrastinine (Figs. 20, 21, and 22, pp. 622 and 623), the corresponding oxidation products of narcotine and hydrastine respectively. The difference finds a sufficient explanation in the fact that whilst all four substances are nearly related, the chain containing the nitrogen atom, which is closed in the two former, is open in the two latter. When, however, hydrastinine is oxidised by means of an aqueous solution of potassium hydroxide, the open chain is closed, and

oxyhydrastinine (Figs. 6 and 7, below), the absorption spectra of which are almost identical with those of corydaldine and  $\omega$ -aminoethylpiperonyl-carboxylic anhydride, is produced (Figs. 20, 21, and 23). The relationship between these compounds is shown by the following formulæ:\*

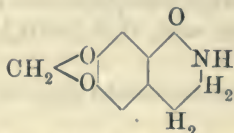


FIG. 4.— $\omega$ -Aminoethylpiperonyl-carboxylic anhydride.

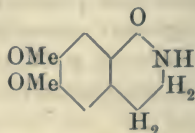


FIG. 5.—Corydaldine.

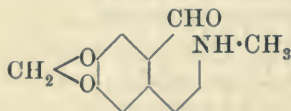


FIG. 6.—Hydrastinine.

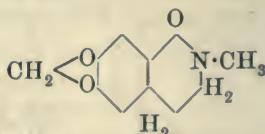


FIG. 7.—Oxyhydrastinine.

Again, when the pyridine ring of cotarnine and hydrastinine is closed by the conversion of these substances into their salts or by their reduction to hydro-derivatives, the changes of structure are reproduced in a striking manner in the spectra. As, however, additional points of considerable interest have arisen in connection with the study of these compounds, we postpone the further discussion of them to a future paper.

We proceed now to consider more fully the influence of specific differences of constitution on the spectra, and to indicate how the relationships established may be used in the study of alkaloids of unknown constitution.

It is now known that many alkaloids which possess the same formula are stereoisomerides. Alkaloids which are related in this way give, like other stereoisomerides, identical spectra (Hartley and Dobbie, *Trans.*, 1900, 77, 498 and 509). Illustrations of this are afforded by *d*-corydaldine and *i*-corydaldine (Fig. 12), narcotine and gnoscopine (Fig. 11), tetrahydroberberine and canadine (Fig. 13). Quinidine (conquinine) and cinchonidine also give absorption spectra identical with those of quinine and cinchonine respectively, of which substances they are probably stereoisomeric forms (Figs. 24 and 25, p. 624). This relationship might sometimes be used to assist the investigation of cases of suspected stereoisomerism. Where, for example, two compounds of

\* Since the above was written, we have found that cotarnine and hydrastinine in alcoholic solution do not possess the constitution commonly assigned to them. This, however, in no way affects the above argument, since there is an important constitutional difference between oxycotarnine and oxyhydrastinine on the one hand, and cotarnine and hydrastinine on the other, whatever formulæ be accepted for the two latter.



the same formula are known, one active and the other inactive, it may be inferred that they are not optical isomerides if they have different absorption spectra.

A case in point is afforded by canadine and papaverine, which possess the same molecular formulae but give widely different absorption spectra. Even if it were not known otherwise that these two substances are structurally different, this might be inferred from the differences in their absorption spectra (Figs. 8 and 13, pp. 616 and 618). Canadine has long been regarded as a stereoisomeride of tetrahydroberberine. This question might have been decided by a comparison of the spectra of the two substances, and with this end in view we had already undertaken their comparison, when Gadamer (*Arch. Pharm.*, 1901, 239, 648) published an account of the resolution of tetrahydroberberine into its active components, and showed that one of them was identical with canadine. The result of the spectroscopic examination points to the same conclusion (Fig. 13, p. 618).

According to Gadamer (*Arch. Pharm.*, 1902, 240, 19), inactive corydaline exists in two modifications, one melting at 134—135°, and the other at 158—159°. The latter of these only can be resolved into *d*- and *i*-corydalines.\* The inactive modification of lower melting point which cannot be resolved, might either be a structural or a stereoisomeric modification of corydaline. The fact that its spectra are identical with those of natural corydaline (Fig. 12) affords strong presumption in favour of the view that the two are structurally identical.

Homologous alkaloids give practically identical spectra. It has been shown from the examination of many homologous substances that the replacement of an atom of hydrogen by a methyl group produces very little effect on the spectra even when the compounds are of low molecular weight (Hartley, *Phil. Trans.*, 1879, Part I, 257). The effect is still less noticeable when the replacement occurs in substances of high molecular weight, such as the alkaloids.

Codeine and morphine (Fig. 26, p. 612) were examined by Hartley (*Phil. Trans.*, 1885, Pt. II, 471), and his curves show clearly the relation between these two compounds. We have examined numerous other cases of homologous alkaloids, and find that they all give practically identical spectra. The curves of corybulbine,  $C_{21}H_{25}O_4N$  (Fig. 27, p. 625), and corydaline,  $C_{22}H_{27}O_4N$  (Fig. 12), and those of quinine,  $C_{20}H_{24}O_2N_2$ , and cupreine,  $C_{19}H_{22}O_2N_2$  (Fig. 24), may be referred to as examples. When, therefore, the formulæ of two alkaloids differ by  $CH_2$ , it may

\* In 1901, we succeeded in resolving *i*-corydaline into its optically active forms, and in separating out the dextro- but not the lævo-modification. We supposed that we had effected the resolution of ordinary corydaline, but the specimen of *i*-corydaline with which we worked may have become, unknown to us, transformed into the modification of higher melting point since described by Gadamer.

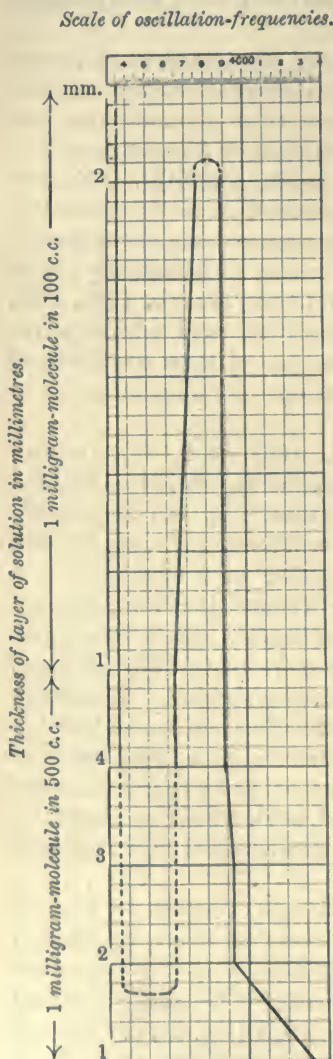


FIG. 26.—*Morphine*,  
 $C_{17}H_{19}O_3N + H_2O$ .  
 (In alcoholic solution.)

*The curve of codeine is identical  
 with this (See also Hartley,  
 loc. cit.).*

be inferred with certainty, if they give dissimilar spectra, that they are not homologous. On the other hand, it cannot be inferred with certainty that two substances which differ by  $CH_2$ , and have very similar spectra, are really homologous, because the difference in the formulæ may be due to other slight structural differences.

The formula of bulbocapnine,  $C_{19}H_{19}O_4N$ , differs from that of papaverine,  $C_{20}H_{21}O_4N$ , and of tetrahydroberberine,  $C_{20}H_{21}O_4N$ , by  $CH_2$ , but the wide difference between the spectra of all three substances (Figs. 28, 8, and 13) renders it highly improbable that bulbocapnine is homologously related to either of the others. What is known of the chemistry of bulbocapnine entirely bears out this conclusion (Gadamer and Ziegenbein, *Arch. Pharm.*, 1902, 240, 81).

Many minor modifications of structure in alkaloids are unaccompanied by any marked difference in the spectra even where the same modifications would produce an appreciable effect on the spectra of compounds of low molecular weight. Corydaline, tetrahydroberberine, and their derivatives afford instances in which the replacement of  $2OCH_3$  by  $CH_2O_2$  does not markedly alter the spectra, and narcotine and hydrastine furnish an example in which the introduction of an additional methoxyl group is unaccompanied by any considerable effect.

The case of cinchotinine and cinchonine may be quoted as another instance. In cinchotinine the side chain  $\cdot CH:CH_2$  of cinchonine is oxidised to a carboxyl group without the spectra being appreciably affected. The resemblance between



the two series of spectra is so close that it would at once suggest a near structural relation of the substances, even if we knew nothing of their chemistry.

The reduction of closed chain compounds is accompanied by a complete change in the character of the spectra (Hartley, *Trans.*, 1885, 47, 691, and Hartley and Dobbie, *Trans.*, 1900, 77, 846). Good illustrations of this are afforded by the widely different spectra of berberine and tetrahydroberberine (Figs. 15 and 13), dehydrocorydaline and corydaline (Figs. 14 and 12), papaverine and tetrahydropapaverine (Figs. 8 and 9). There are, however, cases in which partial reduction produces very little change. Hydroquinine,  $C_{20}H_{26}O_2N_2$ , is unquestionably very closely related to quinine,  $C_{20}H_{24}O_2N_2$ , from which its formula only differs in containing two more atoms of hydrogen. The difference between the spectra of the two substances is hardly perceptible, and it is highly probable, therefore, that the addition of the two atoms of hydrogen is unaccompanied by any important change of structure. The change probably consists in the reduction of the side chain.

From the examination of a large number of alkaloids,\* we believe it may be laid down as a general rule that those which agree closely in structure give similar absorption spectra, whilst those which differ in essential points of structure give dissimilar spectra.

This principle has already been recognised and applied in previous investigations, but it is probably capable of a more extended application in the case of the alkaloids than in that of any other group of substances. This is due to the fact that most of these compounds have a high molecular weight, and changes may be effected in their molecules without alteration of the spectra which, in substances of lower molecular weight, would be attended by wide differences. Thus, the essential identity of constitution subsisting between two alkaloids can often be detected by the spectroscope in spite of differences of structure which, in substances of lower molecular weight, would give rise to spectra so dissimilar that no close chemical relationship between them could be suspected. An example of this is afforded by the absorption spectra of piperonylic and veratric acids, from which no safe conclusion could be drawn as to the relationship of the two substances, whereas a comparison of the absorption spectra of corydaline and tetrahydroberberine, between which the same difference exists, leaves no doubt as to the essential similarity of their structure. Again, cinchonine and cinchotenine give

\* We have made an independent examination of more than thirty alkaloids, including quinine, cinchonine, cinchonidine, cinchonamine, homocinchonidine, quinidine, cupreine, hydroquinine, strychnine, brucine, papaverine, narcotine, gnoscopine, narceine, morphine, codeine, thebaine, laudanine, laudanoline, cryptopine, protopine, hydrastine, canadine, berberine, corydaline, bulbocapnine, corybulbine, corytuberine, and chelidonine.



practically identical spectra, whereas styrolene and benzoic acid, which differ in the same way, give very different spectra. If, therefore, an alkaloid of unknown constitution is found to give spectra closely resembling those of an alkaloid of known constitution, it may with great probability be inferred that the two only differ in the details of their structure.

The study of absorption spectra is thus of real practical value in the investigation of the alkaloids, and we believe that, if systematically used in the manner we have indicated, it might often be the means of saving much time and labour in their chemical investigation, especially in dealing with a large number of closely related compounds such as the lesser known alkaloids of the cinchona bark.

#### EXPERIMENTAL.

For the specimens of the opium alkaloids, including gnoscopine, we are indebted to the kindness of Messrs. T. and H. Smith, of Edinburgh, and for the specimens of oxyhydrastinine and  $\omega$ -aminoethylpiperonyl-carboxylic anhydride, to Professor W. H. Perkin, jun. The specimens of inactive and artificial corydaline, corybulbine, tetrahydroberberine, tetrahydropapaverine, dehydrocorydaline, corydic and berberidic acids, corydaldine, and hydrastinine were prepared in the College laboratory, and our best thanks are due to Messrs. C. K. Tinkler, K. S. Caldwell, and Ed. Jones for assisting in the preparation of some of these substances, and to Mr. C. P. Finn for assisting in photographing the spectra. The remaining alkaloids were obtained by purchase. In every case the specimens were tested as to their purity, and, where necessary, subjected to purification.

Whenever possible, specimens were obtained from at least two distinct sources, and several independent examinations were made of each specimen.

The method adopted in photographing the spectra and in representing them graphically is that employed in the paper on isatin and carbostyryl (Trans., 1899, 75, 640), and fully described in earlier papers by Hartley. In every case, equimolecular solutions were employed. Starting with 1 mill.-mol. in 100 c.c., layers of 5—1 mm. were successively photographed; the solution was then diluted to five times its volume (so that 1 mill.-mol. was then contained in 500 c.c.) and the solution photographed as before. The dilution was continued until the whole spectrum was transmitted. In drawing the curves, the ordinate representing thickness of layer is reduced at each dilution to  $1/5$  of its former size. Each vertical scale division represents, therefore, an equal number of molecules in solution. The abscissæ are reciprocals of wave-lengths. Owing to the slight

solubility of some of the substances examined, it was not always possible to get a solution of 1/100, and thicker layers of a more dilute solution had to be employed. In such cases, for convenience of reference, we have, in drawing the curves, plotted 25 mm. of a solution of 1/500 as equivalent to 5 mm. of a solution of 1/100. Except in the case of hydrastine, all the curves are drawn to the same scale. The position of the transmitted portions of the spectra and of the absorption band have been marked on one of the curves (Fig. 9, p. 616).

The tables of measurements from which the curves were drawn will be included in the next report of the committee of the British Association appointed to investigate the relation between the chemical constitution and the absorption spectra of organic substances.

We may remark that it is difficult by means of curves to give a proper representation of the plates, it being found impracticable to represent adequately differences of intensity as well as extent of absorption upon which the similarity or difference between two plates often to a large extent depends.

By far the most satisfactory comparison is that which is made by the actual inspection of the photographs. When reasonable care is taken to work under similar conditions, the results are remarkably constant. We have never discovered any discrepancy between the photographs of the same preparation, even when taken by different operators at wide intervals of time. Professor Hartley having worked with constant weights and not with molecular quantities of the alkaloids, we have found it necessary, for purposes of comparison, to repeat the examination of a few of the alkaloids which he had previously examined. In so far as it is possible in such cases to compare the results, they show remarkably close agreement.

We gladly avail ourselves of this opportunity to express our thanks to Professor Hartley for lending us the apparatus used in the spectroscopic examination of the alkaloids, as well as for much valuable assistance during the course of the investigation.

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Scale of oscillation-frequencies.

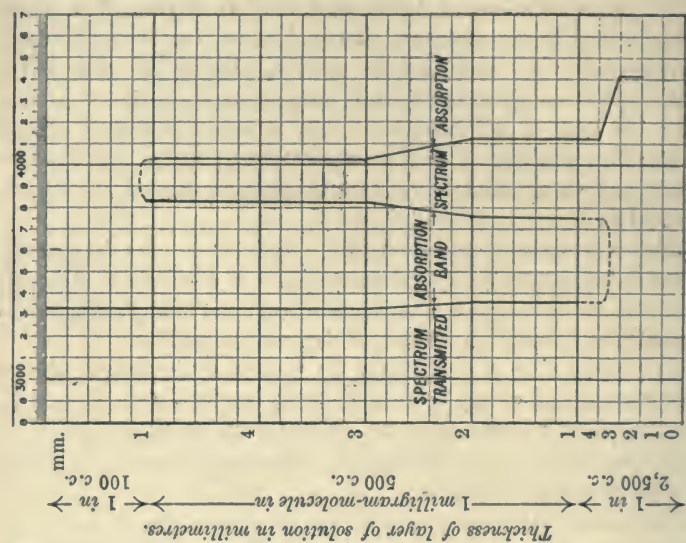


FIG. 9.—Tetrahydropapaverine,  $C_{20}H_{30}O_4N$ .  
(In alcoholic solution.)

Scale of oscillation-frequencies.

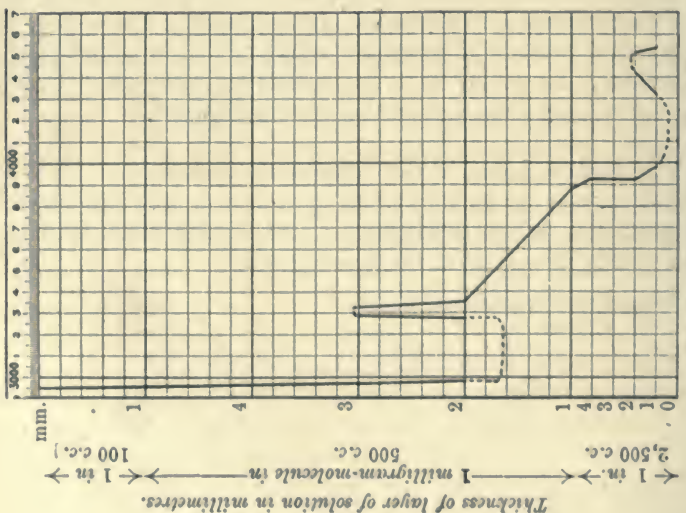


FIG. 8.—Papaverine,  $C_{20}H_{27}O_4N$ .  
(In alcoholic solution.)  
[Cf. Hartley, *Phil. Trans.*,  
1865, Pt. II., 471.]



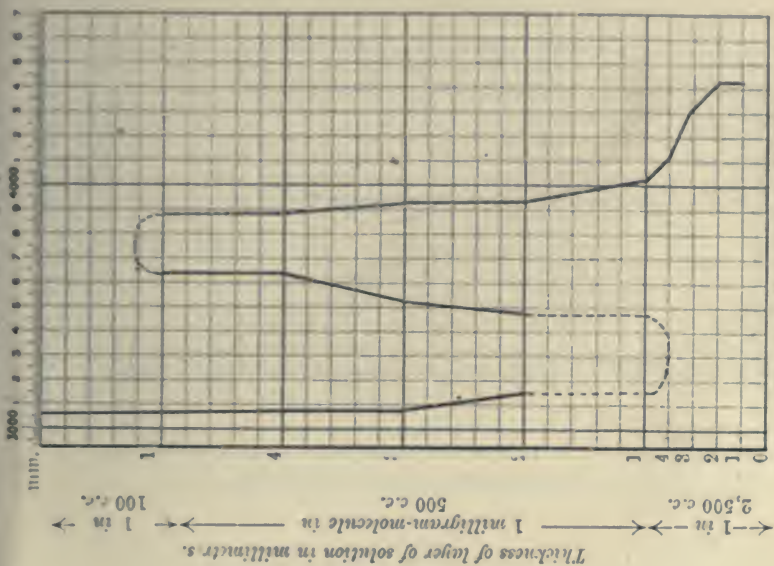


FIG. 10.—Hydrastine,  $C_{21}H_{21}O_6N$ .  
(In alcoholic solution.)

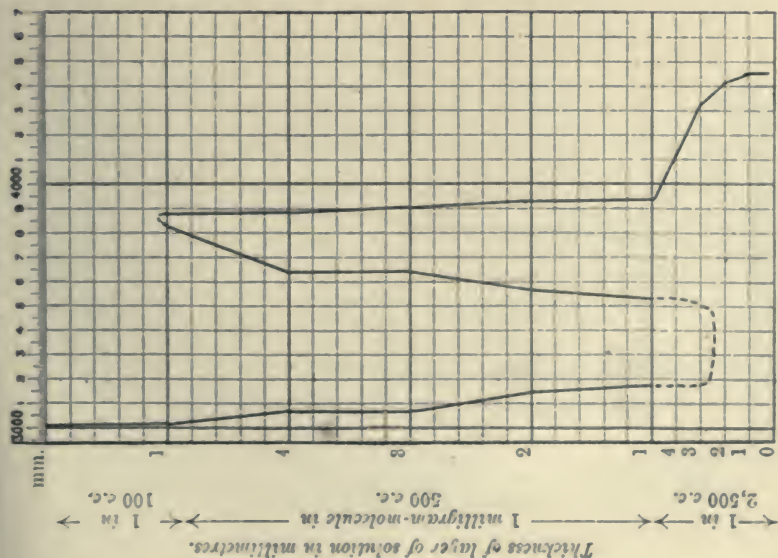


FIG. 11.—Narcotine,  $C_{22}H_{23}O_7N$ .  
(In alcoholic solution.)

(See also Hartley, loc. cit.)  
The curve of gnoscopy is identical with this.

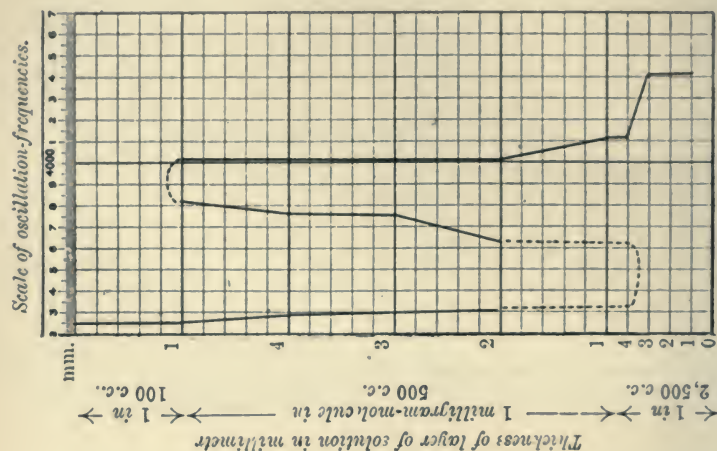


Fig. 13.—Tetrahydroberberine,  $C_{20}H_{21}O_4N$ .  
(In alcoholic solution.)  
The curve of canadine is identical with this.

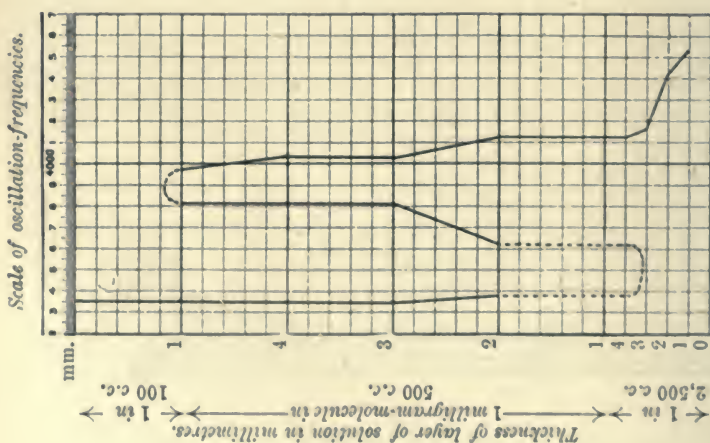


Fig. 12.—Corydaline,  $C_{22}H_{27}O_4N$ .  
The curves of artificial corydaline and  
of i-corydaline are identical with this.  
(In alcoholic solution.)

Scale of oscillation-frequencies.

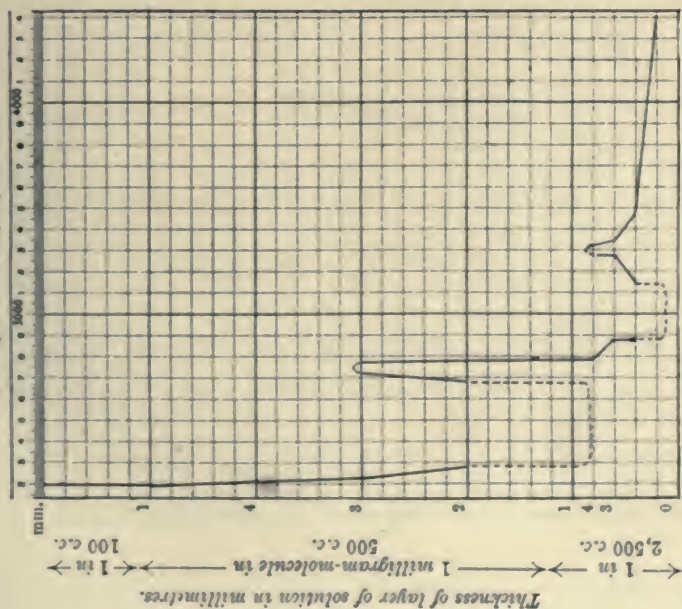


Fig. 14.—Dehydrocorydaline nitrate,  
 $C_{22}H_{23}O_4N \cdot HNO_3 + 2H_2O$ .  
(In aqueous solution.)

Scale of oscillation-frequencies.

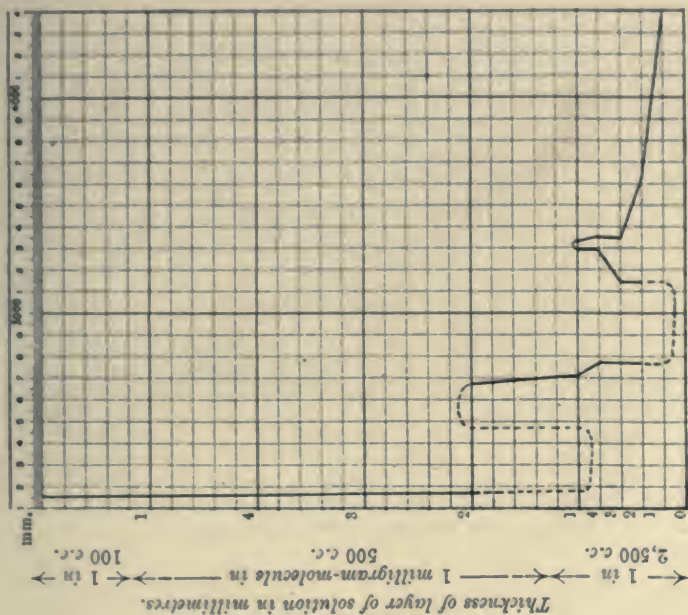


Fig. 15.—Berberine nitrate,  $C_{20}H_{17}O_4N \cdot HNO_3$ ,  
(In aqueous solution.)



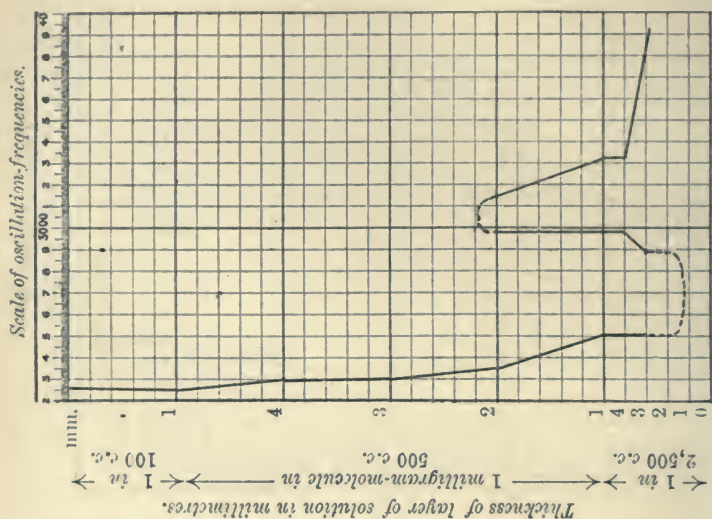


FIG. 17.—Berberic acid,  
 $C_{13}H_7N(CH_3O_2)(CO_2H)_2$   
 (In aqueous solution.)

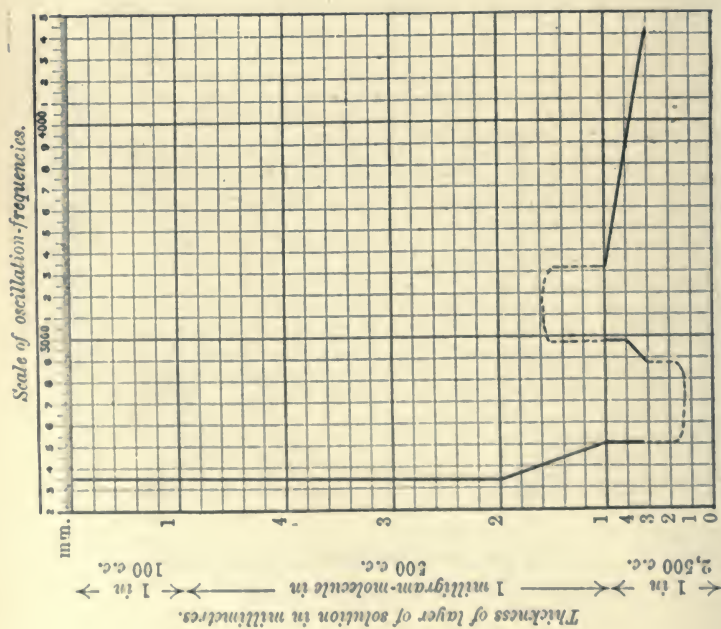


FIG. 16.—Corydic acid,  
 $C_{14}H_9N(OC(H)_2)(CO_2H)_2 + \frac{1}{2}H_2O$ .  
 (In aqueous solution.)

Scale of oscillation-frequencies.

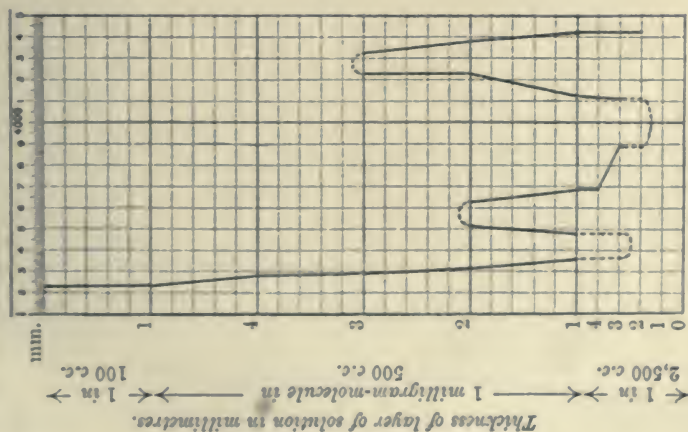


FIG. 18.—*Veratric acid*,  
 $C_6H_3(OCH_2)_2CO_2H + 2H_2O$ .  
*(In alcoholic solution.)*

Scale of oscillation-frequencies.

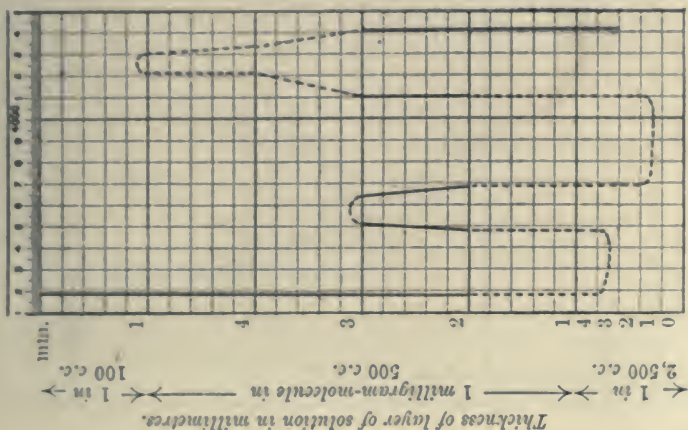


FIG. 19.—*Piperonylic acid*,  
 $C_8H_8(CH_2O)_2CO_2H$ .  
*(In alcoholic solution.)*

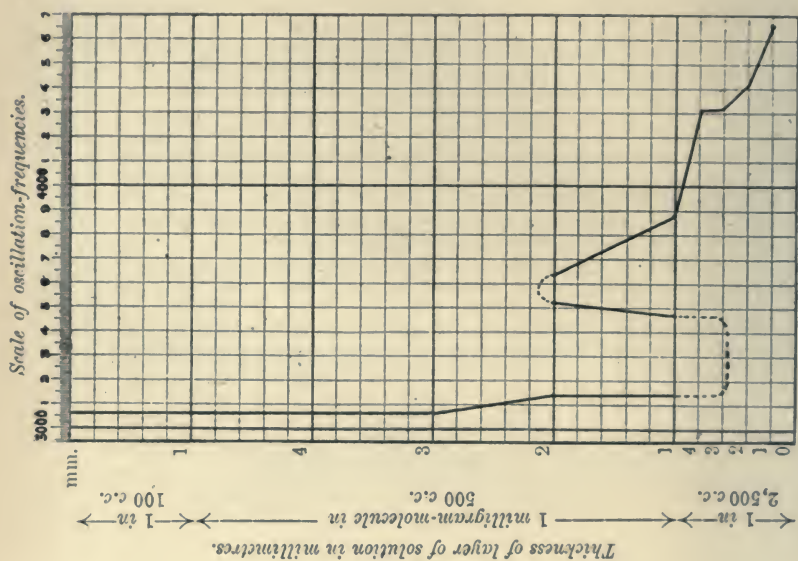


FIG. 21.—*o*-Aminodihydropiperonylcarboxylic anhydride,  $C_9H_7ON(CH_2O)_2$ . (In alcoholic solution.)

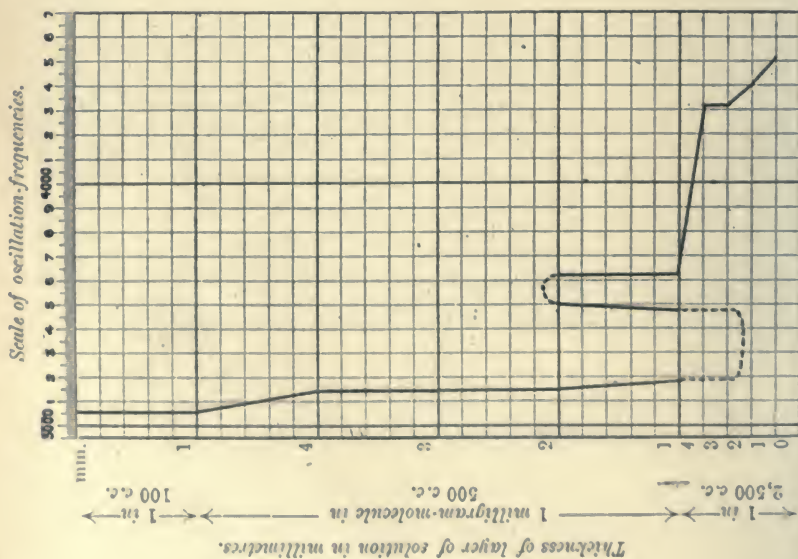


FIG. 20.—Corydaline,  $C_{15}H_{17}ON(OCH_3)_2$ . (In aqueous solution.)



Scale of oscillation-frequencies.

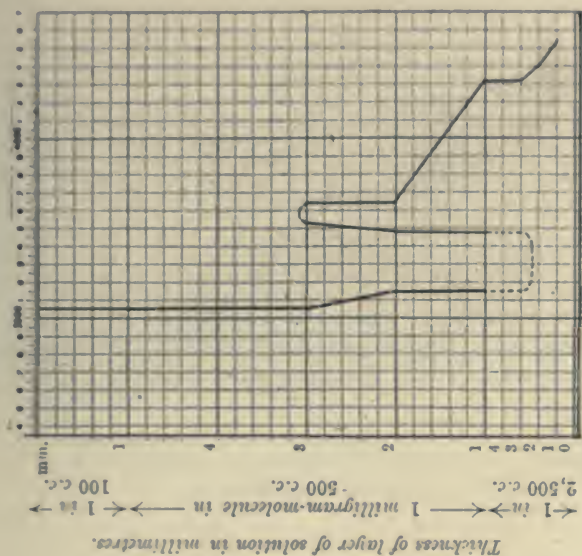


FIG. 23. — *Coryhydrastinine*,  $C_{10}H_9ON(CH_2O_2)$ .  
(In alcoholic solution.)

Scale of oscillation-frequencies.

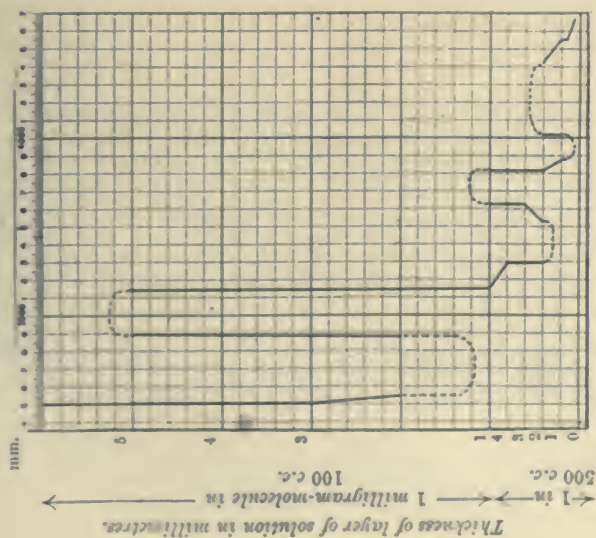


FIG. 22. — *Hydrastinine*,  $C_{11}H_{13}O_5N$ .  
(In alcoholic solution.)

NOTE. — The scale in this case is only one-fifth of the scale on which the other curves are drawn.

Scale of oscillation-frequencies.

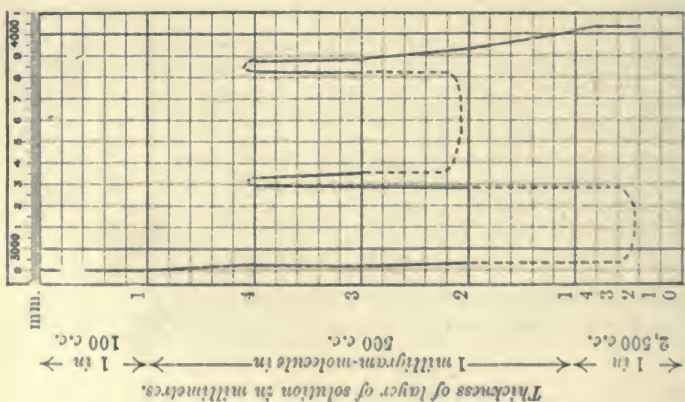


FIG. 24.—Quinine,  $C_{20}H_{24}O_2N_2$ .  
(In alcoholic solution.)  
(See also Hartley, loc. cit.)

The curves of quinidine and cupreine are identical with those of quinine.

Scale of oscillation-frequencies.

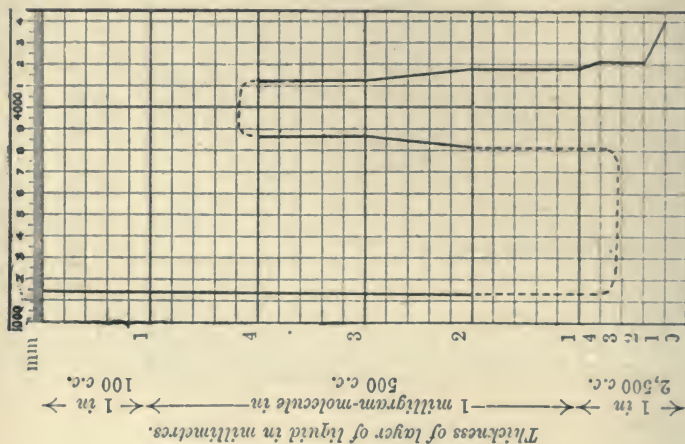


FIG. 25.—Cinchonine,  $C_{19}H_{22}O_2N$ .  
(In alcoholic solution.)  
(See also Hartley, loc. cit.)

The curve of cinchonidine is identical with this.

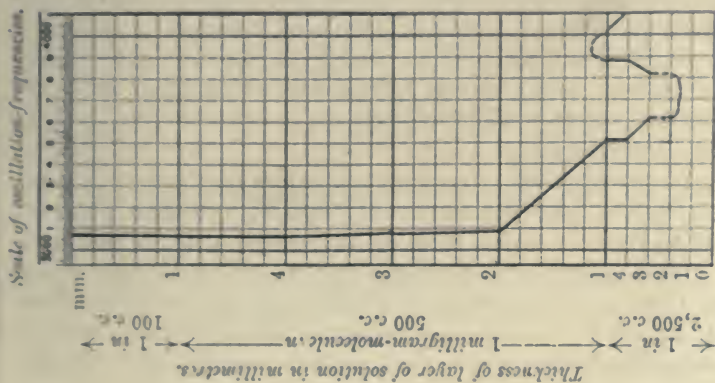


FIG. 28. — *Bulbocapnine*,  $(\text{C}_{11}\text{H}_{19}\text{O}_4\text{N})$ .  
(In alcoholic solution.)

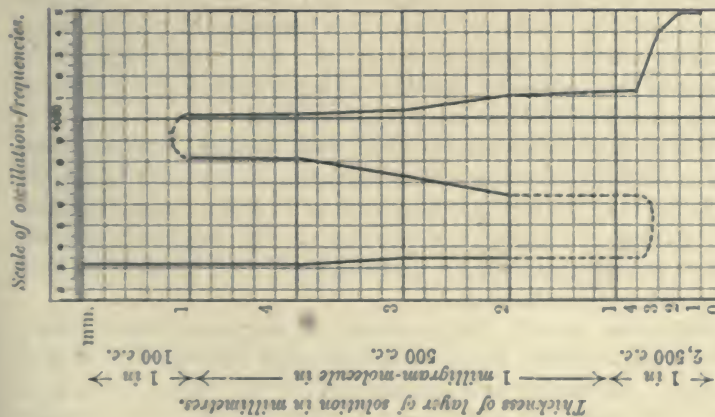


FIG. 27. — *Corybulbine*,  $(\text{C}_{21}\text{H}_{29}\text{O}_4\text{N})$ .  
(In alcoholic solution.)



# LXVI.—*The Absorption Spectra of Laudanine and Laudanosine in Relation to their Constitution.*

By JAMES J. DOBBIE, D.Sc., M.A., and ALEXANDER LAUDER, B.Sc.

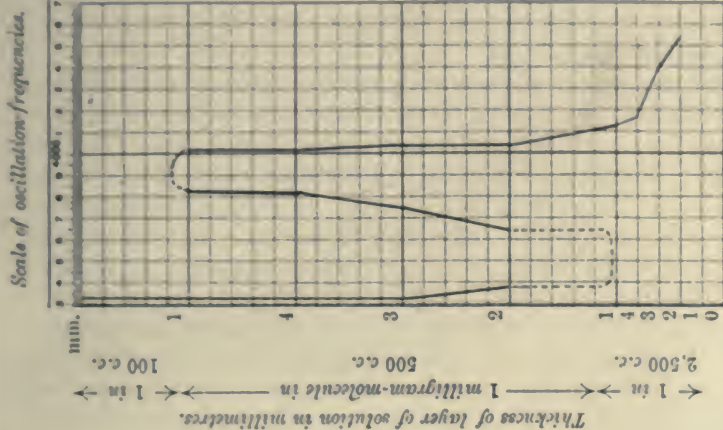
IN the foregoing paper, it has been shown that alkaloids which only differ from one another in minor details of structure give similar spectra, whilst those which differ widely in structure give widely different spectra. So far, no case has yet been encountered in which two substances known to differ substantially in structure give identical or nearly identical spectra.

This principle finds an interesting application in the case of laudanine,  $C_{20}H_{25}O_4N$ , and laudanosine,  $C_{21}H_{27}O_4N$ , two rare alkaloids separated by Hesse (*Annalen*, 1870, 77, 47; *Suppl.*, 1872, 8, 261) from opium. These differ from one another by  $CH_2$ , and since the former contains three, and the latter four methoxyl groups, it has been assumed that the substances are homologous, although the conversion of laudanine into laudanosine has not yet been accomplished. If this view of their relation is correct, they should give practically identical absorption spectra, and this we have found to be actually the case, the measurements of the photographs of the two series of spectra agreeing almost perfectly.

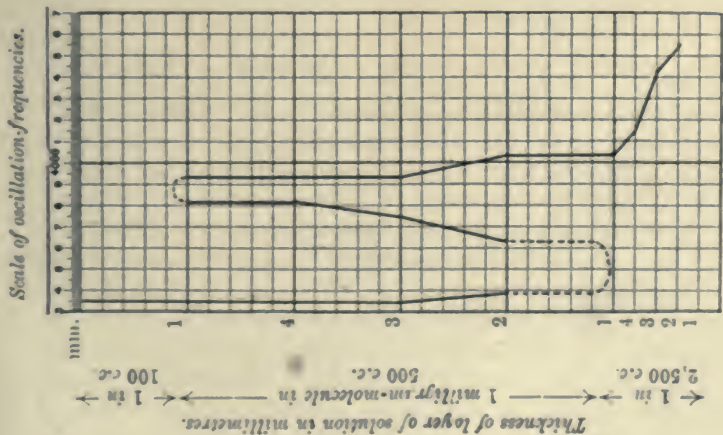
We originally undertook the investigation of these compounds solely with reference to their suspected homology, but we were at once struck, on examining their spectra, with the close resemblance subsisting between them and the spectra of corydaline and tetrahydropapaverine. The photographs of the spectra of corydaline and laudanosine in particular are almost indistinguishable, and suggest a very close structural relation between these two compounds. Laudanosine differs from tetrahydropapaverine by  $CH_2$ , and may simply be a homologue of this substance, possibly having a methyl group attached to carbon atom 4 (Fig. 1) in the preceding paper.

Apart from the closer resemblance of their spectra, however, there is some ground for believing that laudanosine is more nearly related to corydaline than to tetrahydropapaverine. It differs from corydaline only in having one atom of carbon less in its molecule; the two substances cannot therefore be homologous, if the formulæ of both have been correctly determined.

Corydaline has recently been analysed by numerous investigators, with concordant results, and its formula may be regarded as well established. Laudanine and laudanosine, on the other hand, have been but little examined, and there is a possibility that their formulæ may not yet have been definitely settled. Assuming, however, as we are bound to do for the present, that the analyses are correct, cases



Laudanine,  $C_{20}H_{27}O_4N$ .  
(In alcoholic solution.)



Laudanosine,  $C_{21}H_{27}O_5N$ .  
(In alcoholic solution.)

are known in which substances, other than homologues, which are nearly related structurally, show as close an agreement between their spectra even when their formulæ differ more widely than those of corydaline and laudanosine.

Unfortunately, very little is known of the chemistry of laudanosine, but that little is entirely in favour of the view expressed as to its close relationship with corydaline and tetrahydropapaverine. Like those substances, it contains four methyl groups, and yields metahemipinic acid as one of its products of oxidation. It further resembles corydaline in being optically active and in the ease with which, when heated with dilute nitric acid, it undergoes oxidation to a yellow base. This substance, which has not been analysed, may be identical with meconidine (Hesse, *Annalen*, 1870, 77, 47), an alkaloid associated with laudanosine in opium. The formula of meconidine,  $C_{21}H_{23}O_4N$ , bears the same relation to that of laudanosine that the formulæ of dehydrocorydaline and berberine bear to those of corydaline and tetrahydroberberine respectively, as the following table shows:

| <i>Colourless.</i>  | <i>Yellow.</i>  |
|---|---|
| Corydaline,<br>$C_{22}H_{27}O_4N$ ,<br>m. p. 135·5°.        | Dehydrocorydaline,<br>$C_{22}H_{23}O_4N$ ,<br>m. p. 118—120°. |
| Tetrahydroberberine,<br>$C_{20}H_{21}O_4N$ ,<br>m. p. 167°. | Berberine,<br>$C_{20}H_{17}O_4N$ ,<br>m. p. 145°.             |
| Laudanosine,<br>$C_{21}H_{27}O_4N$ ,<br>m. p. 89°.          | Meconidine,<br>$C_{21}H_{23}O_4N$ ,<br>m. p. 58°.             |

Whether the yellow substance produced by the oxidation of laudanosine is identical or not with meconidine, the mere fact of the existence of a coloured base in opium having a formula differing from that of laudanosine by four atoms of hydrogen lends some support to the view of the relationship of these substances set forth in this paper, and this hypothesis receives some additional support from a comparison of the melting points of the substances. The question, however, as to whether laudanosine is more closely related to corydaline or to tetrahydroberberine can only be settled by further chemical investigation.

The point which we wish to emphasise is that it must, from the similarity of its spectra, be built on the same plan as these two closely related compounds.



# ANNUAL GENERAL MEETING,

MARCH 25TH, 1903.

Professor J. EMERSON REYNOLDS, F.R.S., in the Chair.

THE PRESIDENT declared the ballot open for the election of Officers and Council for the ensuing year, Dr. L. T. THORNE and Dr. K. J. P. ORTON being appointed Scrutators. He then presented the following Report on the state of the Society during the past twelve months:

## REPORT OF THE COUNCIL.

The Council have the satisfaction of announcing that the numerical strength of the Society which, on March 26th, 1902, was 2416, is now 2471, the highest number yet reached. Since the last Annual General Meeting, 130 Fellows have been elected and 6 have been reinstated by the Council, making a gross total of 2552. Of these, 27 have been removed for non-payment of two subscriptions, 33 have withdrawn, and 21 have died, making 55 the net increase in the number of Fellows.

By the death of Professor J. Wislicenus, F.R.S., the number of Foreign Fellows has been reduced to 31.

The following Fellows have withdrawn:

|                  |                    |                 |
|------------------|--------------------|-----------------|
| A. Abbott.       | R. H. C. Gompertz. | J. Robinson.    |
| C. Armitage.     | H. W. Gough.       | W. Russell.     |
| W. P. Ashe.      | J. P. Jenkins.     | S. P. Sadtler.  |
| C. R. Blackett.  | T. Judge.          | J. Spilsbury.   |
| H. V. Buttfield. | J. Lunt.           | T. C. Squance.  |
| A. W. Clayden.   | W. B. Mason.       | R. W. Steel.    |
| A. H. Downes.    | C. K. Millard.     | D. R. Steuart.  |
| J. Dunn.         | J. L. Notter.      | W. Taylor.      |
| L. Ehrmann.      | T. H. Page.        | A. Thomson.     |
| G. Evans.        | W. Pullinger.      | Rev. W. Watson. |
| E. I. G. Gill.   | J. C. Quinn.       | C. W. T. Woods. |

The following Fellows have died :

|                                  |                                |   |
|----------------------------------|--------------------------------|---|
| Sir F. A. Abel, Bart.,<br>F.R.S. | Dr. J. H. Gladstone,<br>F.R.S. | Sir W. C. Roberts-<br>Austen, K.C.B.,<br>F.R.S. |
| Dr. C. M. Aikman.                | G. Griffith.                   | Dr. E. Schunck, F.R.S.                          |
| F. B. Bengier.                   | Prof. J. J. Hummel.            | J. Sim.   |
| C. R. Blackett.                  | R. Jackson.                    | W. H. Stanger.                                  |
| Prof. G. Bischof.                | W. I. Macadam.                 | E. Truman.                                      |
| Dr. E. Demarçay.                 | J. Moss.                       | M. Zingler.                                     |
| W. C. Forsyth.                   | J. Robbins.                    |   |
| T. E. Gee.                       |                                |   |

The scientific work of the Society during the past session abundantly testifies to its continued activity. Since the last Annual General Meeting, 189 scientific communications have been made to the Society, 118 of which have already been published in the Transactions, and abstracts of all have appeared in the Proceedings.

The Transactions for 1902 contain 160 memoirs occupying 1604 pages, whilst the volume for the preceding year contains 146 memoirs which occupy 1411 pages. In addition, the volume for 1902 contains the Raoult Memorial Lecture.

The Journal for 1902 contains also 3854 abstracts of papers published mainly in foreign journals, which extend to 1564 pages. These abstracts may be classified as follows :—

#### Part I.

|                         | - Pages. | No. of<br>Abstracts. |
|-------------------------|----------|----------------------|
| Organic Chemistry ..... | 852      | 1632                 |

#### Part II.

|  |       |
|--|-------|
| General and Physical Chemistry .....                         | 409   |
| Inorganic Chemistry .....                                    | 428   |
| Mineralogical Chemistry .....                                | 154   |
| Physiological Chemistry.. .....                              | 421   |
| Chemistry of Vegetable Physiology and Agri-<br>culture ..... | 281   |
| Analytical Chemistry .....                                   | 529   |
|  | <hr/> |
|  | 712   |
|  | <hr/> |
| Total in Parts I and II .....                                | 1564  |
|  | <hr/> |
|  | 3854  |

The Council desires to offer the congratulations of the Society to Professor G. D. Liveing, F.R.S., and to Mr. J. G. Hepburn, who this year reach the Fiftieth Anniversary of their election as Fellows.

The Society has to lament the death of one distinguished Foreign Fellow, Professor J. Wislicenus, F.R.S., and of twenty-one Fellows, amongst whom are two Past Presidents, Sir F. Abel, Bart., F.R.S., and Dr. J. H. Gladstone, F.R.S., who had been Fellows for the long period of fifty-five years; other notable names are those of Sir W. C. Roberts-Austen, K.C.B., F.R.S., Professor J. J. Hummel, and Dr. E. Schunck, F.R.S. Obituary notices of these will appear in the Journal.

The Raoult Memorial Lecture was delivered before a large audience in the Theatre of the Royal Institution (the use of which was kindly granted for the occasion by the Managers) on March 26th, 1902, by Professor J. H. van't Hoff, F.R.S.

The Council are glad to be able to announce that Professor W. H. Perkin, F.R.S., has undertaken to deliver the Wislicenus Memorial Lecture towards the end of the present year.

The Society, in conjunction with the Royal Society and the other Scientific Societies having rooms in Burlington House, arranged for the decoration and illumination of the Building on the occasion of the Coronation of the King.

The plan of holding the Ordinary Meetings of the Society alternately on Wednesdays, at 5.30 p.m., and on Thursdays, at 8 p.m., which was tried for the first time last session, proved so satisfactory that the Council determined to continue the practice during the present session. Both sets of meetings have been equally well attended, and the meetings held on Wednesdays appear, in particular, to suit the convenience of Fellows resident at a distance from London.

The Joint International Committee on Atomic Weights, on which the Society is represented by Professor Thorpe, has issued its first Report. This report, which includes a new table of atomic weights, has been printed in full, both in the Journal and the Proceedings.

The Society having been invited by the Organising Committee of the Fifth International Congress of Applied Chemistry to cooperate with other societies in this country in securing a proper representation of English chemistry, the Council, in June last, appointed a committee to take action in the matter, and have nominated, as its Delegates to represent the Society at the meeting of the Congress in Berlin in June next, the following Fellows: Professor W. A. Tilden, Professor W. R. Dunstan, Professor W. H. Perkin, and Dr. A. Scott.

A petition has been addressed to the Council requesting them to consider the desirability of limiting the period of service of the



Honorary Secretaries and of the Foreign Secretary. The Council having fully considered the matter, passed, *nem. con.*, a resolution stating that whilst the tenure of office should not be indefinitely extended, it was not expedient to fix a definite term of years to the tenure of these offices.

The rapid growth of the Library rendered it imperative that additional accommodation for its extension should be obtained at once. This has been accomplished by utilising for that purpose some of the rooms of the basement, and plans are at present under consideration by which storage accommodation there for the less used books may allow of the normal growth of the Library for another ten or twelve years without its being unduly cramped. This, along with the constantly increasing amount of work entailed by the continuous growth and prosperity of the Society, rendered necessary the rearrangement of the duties of the Staff. After careful consideration, the Council decided to separate the duties of Assistant Secretary from those of the Librarian and Curator, Mr. Steele retaining the latter, whilst Mr. S. E. Carr has been appointed Assistant Secretary.

A complete card catalogue of the Library has now been made, and the new Catalogue, arranged both according to authors and subjects, was issued at the beginning of the present year at the price of half-a-crown. The Library continues to be increasingly used by the Fellows. 925 books were borrowed during the year as against 873 in the previous year. The additions to the Library comprised 64 books. 338 volumes of periodicals, and 23 pamphlets, the corresponding numbers of which in the year before were 153, 441, and 33 respectively. Of the books, 48 have been presented to the Society.

Grants amounting in all to £230 have been made from the Research Fund.

The Council here desires to place on record its high appreciation of the conspicuous services of Professor Dunstan, who now retires from the post of Honorary Secretary which he has held with such advantage to the Society, and who, for the last ten years, has given unsparingly both his time and his energy to the promotion of its highest interests. As one of the Vice-Presidents, the Council hope to have him among them for some time to come.

Another material change in the administrative officers of the Society comes into force with the nomination of the Treasurer, Professor Tilden, to the highest office in the Society, that of President. The Council acknowledges with gratitude the skill and foresight with which, for the last four years, he has controlled the finances of the Society, and it is largely owing to his management, as well as to the ever increasing prosperity of the Society, that the Council has been able to introduce

several important reforms and rearrangements. These are alluded to elsewhere in this report, and it is hoped that they will greatly increase the usefulness of the Society.

Professor W. P. Wynne found it necessary, to the great regret of the Council, to resign the post of Editor of the Journal which he has held for the last four years with such credit to the Society, but kindly consented to act as Editor until the end of 1902, when he was succeeded by Dr. G. T. Morgan, who, in addition to editing the Journal, now edits the Proceedings of the Society.

### REPORT OF THE TREASURER.

The Treasurer, in presenting the balance sheet for the year, stated that the net income was £6212 5s. 1d., whilst the expenses had been £5384 18s., leaving a surplus of £827 7s. 1d., which was about one hundred pounds less than the surplus income in 1902. This was due to several causes, namely, the increase of nearly £380 in the cost of the Journal and Proceedings, the additions to the item of salaries and wages, and the expenses on account of the Collective Index. Whilst, therefore, the present surplus is satisfactory in that it exceeds the amount paid into the account in the form of compositions and admission fees, all these three forms of expenditure will still require careful watching. Three years ago, at the end of his first year as Treasurer, he made an appeal to authors of papers with reference to the preparation of copy for the printers, and he could not help thinking that in the near future more stringent regulations in regard both to the state of the manuscript and the dimensions of papers would have to be imposed with the object of keeping the cost of printing within the means at the disposal of the Society. The Abstracts of foreign and other journals are now indispensable, but, notwithstanding the care exercised by the Sub-Editor, to whom the Society is greatly indebted, and the very moderate remuneration of the excellent body of Abstractors, the cost of their preparation is very heavy.

The amount which will appear in the next balance sheet under the heads of salaries and wages will be somewhat larger, inasmuch as the increase will represent that for an entire year instead of only half a year as on the present occasion. The total cost of the last two volumes of the General Index was £1740, whilst the expenditure on the volume which is in course of preparation has, up to the present, been £204. The greater part of the cost is therefore still to be met. On the other hand, the Library Catalogue is now completed, and for some years there need be no further expense in that form, although

additional accommodation for the books will have to be provided immediately at an outlay which will probably approach £200.

The following tabular statement contains the chief items of income and expenditure during the past four years. The figures represent pounds, the shillings and pence being omitted. It will be seen that whilst the income of the Society is increasing the expenses are growing at nearly the same rate.

|                        | 1900. | 1901. | 1902. | 1903. |
|------------------------|-------|-------|-------|-------|
| Compositions .....     | 110   | 282   | 168   | 299   |
| Admission Fees .....   | 468   | 464   | 652   | 520   |
| Subscriptions .....    | 3510  | 3544  | 3712  | 3957  |
| Sale of Journals ..... | 781   | 880   | 835   | 888   |
| Dividends .....        | 444   | 464   | 476   | 506   |
| Net Income .....       | 5371  | 5668  | 5844  | 6212  |
| <hr/>                  |       |       |       |       |
| Assets .....           | 16710 | 17156 | 17807 | 18446 |
| <hr/>                  |       |       |       |       |
| Expenses ... ..        | 4993  | 4932  | 4913  | 5384  |
| Surplus .....          | 377   | 736   | 930   | 827   |

The Treasurer recalled with satisfaction the sale of Consols previously held by the Society in his first year of office. A serious loss was thus avoided, and, by the reinvestment of the proceeds, a slight addition was secured to the income of the Society.

The estimated values of the securities are all slightly less than at this time last year, but the further investment in May last in £1200 of Leeds Corporation Stock now brings the Assets of the Society to the respectable figure of £18,446 17s. 3d.



THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.

FROM MARCH 22ND, 1902, TO MARCH 21ST, 1903.

Dr.

CR

| 1902.                           | £     | s. | d. | £   | s. | d. |
|---------------------------------|-------|----|----|-----|----|----|
| Mar. 22.                        |       |    |    | 173 | 16 | 10 |
| Balance at Bank, March 22, 1902 |       |    |    |     |    |    |
| Year's Dividends on £4,400      |       |    |    |     |    |    |
| Metropolitan Board of Works     |       |    |    |     |    |    |
| 3½ per cent. Stock              | 144   | 10 | 10 |     |    |    |
| Year's Dividends on £1,000      |       |    |    |     |    |    |
| North British Railway 4 per     |       |    |    |     |    |    |
| cent. No. 1 Preference Stock    | 37    | 12 | 3  |     |    |    |
| Year's Dividends on £1,034      |       |    |    |     |    |    |
| Great Western Railway 2½ per    |       |    |    |     |    |    |
| cent. Debenture Stock           | 24    | 5  | 3  |     |    |    |
|                                 |       |    |    | 206 | 8  | 4  |
| Repayment of Unexpended Grants  |       |    |    |     |    |    |
| Repayment of Income Tax         |       |    |    | 1   | 10 | 11 |
|                                 |       |    |    | 12  | 7  | 10 |
| 1903.                           |       |    |    |     |    |    |
| Mar. 21.                        |       |    |    |     |    |    |
| Balance at Bank                 | 164   | 3  | 11 |     |    |    |
| £4,400 Metropolitan Board of    |       |    |    |     |    |    |
| Works 3½ per cent. Stock        | 4664  | 0  | 0  |     |    |    |
| £1,000 North British Railway    |       |    |    |     |    |    |
| 4 per cent. No. 1 Preference    |       |    |    |     |    |    |
| Stock                           | 1260  | 0  | 0  |     |    |    |
| £1,034 Great Western Railway    |       |    |    |     |    |    |
| 2½ per cent. Debenture Stock    | 868   | 11 | 0  |     |    |    |
|                                 | £6056 | 14 | 11 |     |    |    |
|                                 | £394  | 3  | 11 |     |    |    |

Audited with vouchers  
and found correct.  
21st March, 1903.

## THE TREASURER IN ACCOUNT WITH THE CHEMICAL

Dr.

|   | £    | s. | d. | £ | s. | d. | £    | s. | d.       |
|---|------|----|----|---|----|----|------|----|----------|
| Balance at Bank, March 22nd, 1902 .....   | 2034 | 0  | 9  |   |    |    |      |    |          |
| „ in hands of Treasurer .....   | 0    | 4  | 3  |   |    |    |      |    |          |
| Transferred from Deposit Account (October 9th, 1902).....   |      |    |    |   |    |    | 2034 | 5  | 0        |
| Receipts by Life Compositions, Admission Fees and Subscriptions from March 22nd, 1902, to March 21st, 1903 :— |      |    |    |   |    |    | 500  | 0  | 0        |
| Life Compositions—7 at £30, 2 at £20, 1 at £15, 2 at £12, 1 at £10 .....                                      | 299  | 0  | 0  |   |    |    |      |    |          |
| Admission Fees .....  | 520  | 0  | 0  |   |    |    |      |    |          |
| 1 Subscription for 1898 at £2 .....   | 2    | 0  | 0  |   |    |    |      |    |          |
| 2 Subscriptions „ 1899 „ £2 .....   | 4    | 0  | 0  |   |    |    |      |    |          |
| 3 „ „ 1900 „ £2 .....   | 6    | 0  | 0  |   |    |    |      |    |          |
| 86 „ „ 1901 „ £2 .....  | 172  | 0  | 0  |   |    |    |      |    |          |
| 5 „ „ 1902 „ £1 .....   | 5    | 0  | 0  |   |    |    |      |    |          |
| 559 „ „ „ „ £2 .....  | 1178 | 0  | 0  |   |    |    |      |    |          |
| 6 „ „ 1903 „ £1 .....   | 6    | 0  | 0  |   |    |    |      |    |          |
| 1291 „ „ „ „ £2 .....   | 2582 | 0  | 0  |   |    |    |      |    |          |
| 1 „ „ 1904 „ £2 .....   | 2    | 0  | 0  |   |    |    |      |    |          |
| Sale of Journals .....  | 723  | 3  | 0  |   |    |    | 4776 | 0  | 0        |
| „ Proceedings .....   | 12   | 15 | 6  |   |    |    |      |    |          |
| „ General Index .....   | 21   | 6  | 8  |   |    |    |      |    |          |
| „ Memorial Lectures .....   | 28   | 16 | 9  |   |    |    |      |    |          |
| „ Library Catalogue .....   | 22   | 7  | 6  |   |    |    |      |    |          |
| „ Jubilee Volume .....  | 1    | 2  | 0  |   |    |    |      |    |          |
| Proceeds of Advertisements in Journal .....   | 79   | 6  | 3  |   |    |    | 888  | 17 | 8        |
| Subscription from the Society of Chemical Industry to June, 1902...   | 8    | 8  | 0  |   |    |    |      |    |          |
| „ „ „ Public Analysts to January 1st, 1903 .....  | 12   | 12 | 0  |   |    |    |      |    |          |
| „ „ „ Physical Society to January 1st, 1903 .....   | 19   | 8  | 6  |   |    |    | 40   | 8  | 6        |
| Repayment of Income Tax .....   | 26   | 9  | 0  |   |    |    |      |    |          |
| Year's Dividends on £6,730 Metropolitan Board of Works 3½ per cent. Stock .....                               | 221  | 1  | 7  |   |    |    |      |    |          |
| „ „ £1,050 London and North-Western Railway Debenture Stock .....   | 29   | 11 | 3  |   |    |    |      |    |          |
| „ „ £1,520 14s. 3d. Cardiff Corporation Stock.....  | 42   | 15 | 6  |   |    |    |      |    |          |
| „ „ £1,400 India 2½ per cent. Stock.....  | 32   | 17 | 1  |   |    |    |      |    |          |
| „ „ £2,858 Midland 2½ per cent. Preference .....  | 55   | 6  | 7  |   |    |    |      |    |          |
| „ „ £2,400 Bristol 2½ per cent. Debenture .....   | 56   | 5  | 0  |   |    |    |      |    |          |
| „ „ £1,200 Leeds 3 per cent. Stock .....  | 28   | 2  | 6  |   |    |    |      |    |          |
| Interest on Bank Deposit .....  | 14   | 10 | 5  |   |    |    | 506  | 18 | 11       |
|   |      |    |    |   |    |    |      |    | 6212 5 1 |

## Assets.

|   | Estimated Value. |
|---|------------------|
| March 21st, 1903.   | £ s. d.          |
| Balance at Bank (Current Account) .....                       | 1707 9 1         |
| „ „ (on Deposit) .....  | 1000 0 0         |
| „ in hands of Treasurer .....                                 | 1 2 0            |
| £6,730 Metropolitan Board of Works 3½ per cent. Stock         | 7133 10 0        |
| £1,050 London and North-Western Railway Debenture Stock ..... | 1060 10 0        |
| £1,520 14s. 3d. Cardiff Corporation 3 per cent. Stock...      | 1444 13 6        |
| £2,858 Midland Railway 2½ per cent. Preference .....          | 1815 13 4        |
| £2,400 Bristol Corporation 2½ per cent. Debenture Stock       | 1044 0 0         |
| £1,400 India 2½ per cent. Stock .....                         | 1193 13 4        |
| £1,200 Leeds Corporation 3 per cent Stock.....                | 1146 0 0         |
|   | £18,446 17 3     |

SOCIETY, FROM MARCH 22ND, 1902, TO MARCH 21ST, 1903.

CR.

*Expenses on Account of the Journal and Proceedings.*

|                                     | £    | s. | d. | £ | s. | d. | £    | s. | d. |
|-------------------------------------|------|----|----|---|----|----|------|----|----|
| Salary of Editor                    | 302  | 10 | 0  |   |    |    |      |    |    |
| " Sub-Editor                        | 200  | 0  | 0  |   |    |    |      |    |    |
| " Indexer                           | 80   | 0  | 0  |   |    |    |      |    |    |
| Editorial Postages                  | 15   | 9  | 7  |   |    |    |      |    |    |
| Abstractors' Fees                   | 383  | 7  | 1  |   |    |    |      |    |    |
| Printing of Journal                 | 1928 | 18 | 0  |   |    |    |      |    |    |
| Printing of Advertisements          | 20   | 17 | 2  |   |    |    |      |    |    |
| Printing Wrappers                   | 90   | 14 | 0  |   |    |    |      |    |    |
| Distribution of Journal by Printers | 429  | 18 | 7  |   |    |    |      |    |    |
| " Society                           | 14   | 19 | 7  |   |    |    |      |    |    |
| Authors' Copies                     | 102  | 0  | 3  |   |    |    |      |    |    |
| Illustrations for Journal           | 32   | 4  | 2  |   |    |    |      |    |    |
|                                     |      |    |    |   |    |    | 3578 | 18 | 5  |
| Printing of Proceedings             | 184  | 5  | 8  |   |    |    |      |    |    |
| Distribution of Proceedings         | 50   | 14 | 11 |   |    |    |      |    |    |
|                                     |      |    |    |   |    |    | 235  | 3  | 7  |
| Publisher's Commission              | 77   | 18 | 2  |   |    |    |      |    |    |
| Advertising Agent's Commission      | 11   | 18 | 0  |   |    |    |      |    |    |
|                                     |      |    |    |   |    |    | 89   | 16 | 2  |

*Expenses on Account of Collective Index 1893—1902.*

|                |     |    |    |  |  |  |     |   |   |
|----------------|-----|----|----|--|--|--|-----|---|---|
| Salaries       | 126 | 10 | 0  |  |  |  |     |   |   |
| Petty expenses | 1   | 2  | 6  |  |  |  |     |   |   |
| Index Stips    | 4   | 11 | 10 |  |  |  |     |   |   |
|                |     |    |    |  |  |  | 132 | 4 | 4 |

*Expenses on Account of the Library Catalogue.*

|                           |    |    |   |  |  |  |    |    |   |
|---------------------------|----|----|---|--|--|--|----|----|---|
| Gratuity to Assistant     | 10 | 0  | 0 |  |  |  |    |    |   |
| Cards and Numbering Stamp | 4  | 18 | 0 |  |  |  |    |    |   |
|                           |    |    |   |  |  |  | 14 | 18 | 0 |

*Expenses on Account of the Library.*

|                             |     |    |    |  |  |  |     |    |    |
|-----------------------------|-----|----|----|--|--|--|-----|----|----|
| Salary of Library Assistant | 12  | 17 | 6  |  |  |  |     |    |    |
| Books and Periodicals       | 211 | 19 | 6  |  |  |  |     |    |    |
| Binding                     | 76  | 13 | 10 |  |  |  |     |    |    |
|                             |     |    |    |  |  |  | 301 | 10 | 10 |

*House Expenses.*

|   |      |    |    |     |      |    |   |
|---|------|----|----|-----|------|----|---|
| Providing Refreshments  | 23   | 13 | 11 |     |      |    |   |
| Lighting the Building..... (Gas, £21 18s. 7d.; Electric Light, £21 19s. 8d.)                            | 43   | 18 | 3  |     |      |    |   |
| Heating the Building  | 17   | 3  | 0  |     |      |    |   |
| Cleaning  | 8    | 2  | 6  |     |      |    |   |
| Repairs   | 70   | 0  | 1  |     |      |    |   |
| Petty House Expenses  | 88   | 5  | 5  |     |      |    |   |
| House Porter's Wages  | 63   | 15 | 0  |     |      |    |   |
| Commissionaire's Wages  | 35   | 17 | 0  |     |      |    |   |
| Gratuities  | 2    | 19 | 6  |     |      |    |   |
| Inhabited House Duty  | 3    | 2  |    |     |      |    |   |
|   |      |    |    | 323 | 18   | 7  |   |
| Salary of Librarian and Corator   | 200  | 0  | 0  |     |      |    |   |
| Salary of Assistant Secretary   | 62   | 10 | 0  |     |      |    |   |
| Pension to Mr. Hall   | 130  | 0  | 0  |     |      |    |   |
| Office Assistance   | 3    | 19 | 0  |     |      |    |   |
| Miscellaneous Printing  | 69   | 14 | 3  |     |      |    |   |
| List of Fellows   | 48   | 8  | 6  |     |      |    |   |
| Bye-laws  | 8    | 15 | 0  |     |      |    |   |
| Stationery  | 53   | 7  | 3  |     |      |    |   |
| Indexing for International Catalogue  | 30   | 0  | 0  |     |      |    |   |
| Coronation Decorations  | 15   | 0  | 0  |     |      |    |   |
| Advertisements  | 4    | 17 | 8  |     |      |    |   |
| Office Furniture  | 19   | 1  | 4  |     |      |    |   |
| Bank Charges  | 1    | 1  | 3  |     |      |    |   |
| Treasurer's Petty Cash Disbursements  | 7    | 10 |    |     |      |    |   |
| " Assistant   | 20   | 0  | 0  |     |      |    |   |
| Postage Account: Office Postages, £33 13s. 6d.; Postal Cards and Stamped Envelopes (Clay), £17 12s. 4d. | 51   | 5  | 10 |     |      |    |   |
|   |      |    |    |     | 5394 | 18 | 0 |
| Purchase of £1200 Leeds 3 per cent. Stock   | 1143 | 1  | 0  |     |      |    |   |
| Transferred to Deposit Account (February 18th, 1903)  | 500  | 0  | 0  |     |      |    |   |
| Balance at Bank   | 1707 | 9  | 1  |     |      |    |   |
| " in hands of Treasurer   | 1    | 2  |    |     |      |    |   |

£6746 10 1Audited with vouchers and  
found correct.LEONARD TEMPLE THORNE.  
J. T. HEWITT.  
K. J. P. ORTON.

21st March, 1903.



The TREASURER, in concluding, proposed a vote of thanks to the Auditors, which was acknowledged by Dr. L. T. THORNE.

Professor DEWAR proposed a vote of thanks to the Treasurer, Secretaries, and Council. The motion was seconded by Professor W. H. PERKIN, and unanimously adopted. Professor DUNSTAN responded.

The PRESIDENT then delivered his Address to the Society, which will be found on pp. 639—650.

Dr. RUSSELL, in moving the adoption of the report, proposed a vote of thanks to the President, coupled with a request that he would allow his address to be printed in the Transactions.

Professor THORPE seconded the motion, which was carried by acclamation.

After the President had returned thanks, the Scrutators presented their report to the President, when he declared the following to have been duly elected as Officers and Council for the ensuing session :—

*President* : W. A. Tilden, D.Sc., F.R.S.

*Vice-Presidents who have filled the office of President* : H. E. Armstrong, Ph.D., LL.D., F.R.S. ; A. Crum Brown, D.Sc., LL.D., F.R.S. ; Sir W. Crookes, F.R.S. ; James Dewar, M.A., LL.D., F.R.S. ; A. Vernon Harcourt, M.A., D.C.L., F.R.S. ; H. Müller, Ph.D., LL.D., F.R.S. ; W. Odling, M.A., M.B., F.R.S. ; W. H. Perkin, Ph.D., LL.D., F.R.S. ; J. Emerson Reynolds, Sc.D., M.D., F.R.S. ; Sir H. E. Roscoe, LL.D., F.R.S. ; W. J. Russell, Ph.D., F.R.S. ; T. E. Thorpe, C.B., LL.D., F.R.S. ; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents* : Wyndham R. Dunstan, M.A., F.R.S. ; P. F. Frankland, LL.D., F.R.S. ; David Howard ; Herbert McLeod, F.R.S. ; Raphael Meldola, F.R.S. ; H. A. Miers, D.Sc., F.R.S.

*Secretaries* : A. Scott, M.A., D.Sc., F.R.S. ; W. P. Wynne, D.Sc., F.R.S.

*Foreign Secretary* : Sir W. Ramsay, K.C.B., LL.D., F.R.S.

*Treasurer* : Horace T. Brown, LL.D., F.R.S.

*Other Members of Council* : J. J. Dobbie, M.A., D.Sc. ; Augustus E. Dixon, M.D. ; M. O. Forster, Ph.D., D.Sc. ; A. Harden, D.Sc., Ph.D. ; J. T. Hewitt, M.A., D.Sc. ; C. A. Kohn, Ph.D., B.Sc. ; J. E. Marsh, M.A. ; E. J. Mills, D.Sc., LL.D., F.R.S. ; S. U. Pickering, M.A., F.R.S. ; S. Ruhemann, M.A., Ph.D. ; J. A. Voelcker, Ph.D. ; James Walker, D.Sc., F.R.S.

The proceedings then terminated.

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## PRESIDENTIAL ADDRESS TO THE CHEMICAL SOCIETY.

Delivered at the ANNUAL GENERAL MEETING, MARCH 25TH, 1903.

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

Introductory—State of the Society—Reports of Progress in Research—Centenary of Promulgation of Dalton's Atomic Theory—Inorganic Research—Inorganic Isomerism—Catalysis and Inorganic Ferments.

At the termination of this my second and last year of office as President, it is again my agreeable duty to congratulate the Fellows on the prosperity of the Society. The number of Fellows has increased to 2471. The income of the Society has reached the satisfactory total of £6212, and the Papers communicated to the Society since the last Anniversary meeting has risen to 189. Without having to chronicle any epoch-making discoveries during the year, it may be safely said that important progress has been made by the Fellows in the researches which have appeared in our Transactions.

In the midst of these causes for congratulations we must yet feel profound sorrow that death has been unusually busy in the ranks of our Society, both among the aged and venerable leaders in science, and among the younger and more vigorous. Sir Frederic Abel, Dr. John H. Gladstone, and Dr. Schunck have passed away from among us full of years and honours, leaving behind them memories of great pioneer work well and nobly done in three distinct branches of our science. We have also to mourn the loss of Sir W. C. Roberts-Austen, whose genial presence we shall sorely miss; of Mr. George Griffith, whose invaluable services to science as Organising Secretary of the British Association will be long remembered, and of Professor Hummel, in whom an important branch of applied chemistry has lost one of its scientific leaders.

The Council hope to publish suitable obituary notices of all these distinguished Fellows, and I am glad to be able to announce that Professor W. H. Perkin, jun., has kindly undertaken to deliver a Memorial Lecture of our illustrious Foreign Fellow, Professor Wislicenus, who has also passed away during the year.

I have much pleasure in congratulating Professor Liveing, F.R.S., and Mr. J. G. Hepburn, LL.D., on attaining their jubilee as Fellows of the Society.

*Reports on Progress in Research.*

On several occasions of late years I have drawn attention to the great need of reports on the history and progress of special branches of research by experts in the particular lines of investigation. Without such aids it is becoming increasingly difficult for those engaged in other directions to properly appreciate the bearing of new work on the progress made in particular departments; I have, therefore, special pleasure in drawing attention to two able reports of the desired kind which have been presented to, and published by, the British Association for the Advancement of Science during the last year.

Dr. Crossley's report "On Hydroaromatic Compounds with Single Nucleus" refers to the most important memoirs on the subject with which he is so highly qualified to deal, and, while making clear the present position of this attractive field of research, it is no less suggestive as to the direction of further work. The new editor of our Transactions, Dr. G. T. Morgan, is the author of another excellent report (also published by the British Association) on "Our present knowledge of aromatic diazo-compounds." So many of our Fellows have taken leading parts in the development of this far-reaching line of research that the adequate treatment of the subject by Dr. Morgan has a special interest for us.

I hope that other topics of importance may be similarly treated in the future.

*Centenary of Dalton's Statement of his Atomic Theory.*

I need scarcely remind the Fellows that this year is the centenary of the announcement, in a tentative form, of probably the most fruitful and valuable of all scientific hypotheses—Dalton's Atomic Theory. On the 21st of October, 1803, Dalton read a paper "On the Absorption of Gases by Water and other Liquids" before a select audience of nine members of the Literary and Philosophical Society of Manchester. He appended to that paper a statement which, according to Sir Henry Roscoe and Dr. Harden,\* is the first published indication of the atomic theory, although the paper was not circulated in the Manchester *Memoirs* until November, 1805. Thus, just 100 years ago, the conception of the discrete nature of matter was formulated, and used to explain the facts then known as to the constant composition of chemical compounds, and the laws discovered by Dalton as to their formation in definite and multiple proportions. This germ of the

\* *A New View of the Origin of Dalton's Atomic Theory.* Macmillan and Co. 1896.



molecular theory of matter, which now pervades all thought in chemistry and physics, arose, as Nernst truly says, "by a single effort of modern science, like a Phoenix from the ashes of the old Greek philosophy." Therefore, physicists as well as chemists are interested in an event of the highest significance in the development of both branches of science. I am glad to know that a special celebration will shortly be held in that great city which claims Dalton as her illustrious son.

### *Inorganic Research.*

On looking over the volumes of our Transactions for the last two years, 1901 and 1902, I find that the number of memoirs published were respectively 146 and 160, showing a satisfactory increase in activity during last year. Of the total 306 memoirs:

248 recorded researches in Organic Chemistry.

24       "       "       Physical Chemistry.

29       "       "       Inorganic Chemistry.

5       "       "       Analytical Chemistry.

I cannot avoid regarding these statistics as unsatisfactory from one point of view, inasmuch as they indicate that the great inorganic division of the science is very inadequately represented. Far be it from me to suggest that there should be any diminution of activity in organic research, notwithstanding our knowledge of at least 75,000 carbon compounds, for many problems of high importance still await solution in that division of the science. Neither do I desire the mere multiplication of inorganic substances, unless their formation tends to a definite end in the recognition of new relations, analogies, or capacities among the fifty or more best known elements. Rather what I plead for is that more comprehensive study of the compounds of the elements which is represented by the term "comparative chemistry."

The line which is likely to be of most interest to those trained in the methods of organic investigation is that of the comparison of other elements with carbon in regard to their power of building up more or less complex molecules. All polyvalent elements possess this power in some degree, and many problems as to the constitution of compounds of even comparatively simple character require further investigation; but there are few inquiries of this kind of greater interest than those involving *Isomerism*, which was for long considered to be peculiar to compounds of carbon.

*Inorganic Isomerism.*

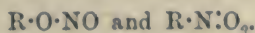
Closer study of the constitution of compounds of other elements than carbon has gradually brought to light a number of cases of inorganic isomerism. These are examples, as clear as any met with in organic chemistry, of compounds which have the same composition, but differ in characters and also in molecular complexity or in structure. The number of these cases will probably be much increased as our knowledge of the constitution of inorganic compounds progresses. The existence of isomerism of the kind in question is, however, either completely ignored or only slightly mentioned in the most recent and advanced text-books of inorganic chemistry with which I am acquainted. I therefore propose to occupy a portion of the short time at my disposal in bringing together the principal examples of inorganic isomerism hitherto met with, in the hope of stimulating further investigation in that direction.

Molecular condensation or polymerism is well known to be common among inorganic compounds, as in the familiar examples of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ,  $\text{VO}_2$  and  $\text{V}_2\text{O}_4$ ,  $\text{VS}_2$  and  $\text{V}_2\text{S}_4$ ,  $\text{NbO}_2$  and  $\text{Nb}_2\text{O}_4$ ,  $\text{TaO}_2$  and  $\text{Ta}_2\text{O}_4$ . Only in the cases of the oxides of nitrogen can the changes of molecular complexity be traced through changes of gas density; in the other instances, the evidence is necessarily indirect. Again, polymerism is recognisable in the oxides of silicon, tin, titanium, tungsten, molybdenum, chromium, &c., but in these cases the evidence is still less direct as to the extent of molecular condensation. I am well aware that many chemists do not admit that polymerism is a form of isomerism, and restrict the latter term to the cases of substances which have not only the same composition but also the same molecular weight; however, in attaching so little importance to the existence of polymerism, there appears to be a risk of missing the recognition of important relationships. It must be remembered that some carbon compounds of fundamental importance can result from polymerisation, for example, benzene,  $\text{C}_6\text{H}_6$ , is a polymeride of acetylene,  $\text{C}_2\text{H}_2$ , and can actually be formed from the latter by the action of heat. The many points of resemblance between silicon and carbon are well known, but they are materially modified by the greater attraction of silicon for oxygen than for hydrogen. Now, it is highly probable, from considerations of the very low volatility of ordinary silicon dioxide as compared with  $\text{SiCl}_4$ , and the high volatility of carbon dioxide as compared with its chloride, that silica is a polymeride of  $\text{SiO}_2$ ; and the frequency with which we meet with  $\text{Si}_6$ , as well as  $\text{Si}_3$ ,  $\text{Si}_4$ , and even  $\text{Si}_9$  among the most probable formulæ of native silicates suggests the possibility of some of them being derivatives of a benzenoid condensation product of

$6\text{SiO}_2$ . I merely suggest this in order to indicate that inorganic polymerism may mean much more than is commonly supposed; but the cases which I now desire to consider briefly are those of isomerides in the restricted sense of the term.

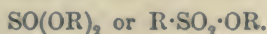
Among the most familiar cases of isomerism are the nitrites and sulphites.

The empirical formula  $\text{RNO}_2$  is common to the two possible isomeric compounds



Salts of the first type, which are true nitrites, are probably those of the alkali metals obtained by neutralising free nitrous acid with sodium and other hydroxides. The silver salt is, on the contrary, more of the imide type,  $\text{Ag}\cdot\text{N}:\text{O}_2$ . The substitution of an alcohol radicle for the metal in each case brings out the distinction between them more clearly. The sodium salt is well known to give, with ethyl alcohol and sulphuric acid, a liquid which boils at  $18^\circ$ , and comports itself in all other respects as the ester  $\text{C}_2\text{H}_5\text{O}\cdot\text{NO}$ . The silver salt, when treated with ethyl iodide, gives a liquid boiling at  $114^\circ$ , and acting towards alkalis and nascent hydrogen as  $\text{C}_2\text{H}_5\cdot\text{N}:\text{O}_2$ . Divers is disposed to consider all nitrites as compounds of the imide type, but in view of the facts cited it appears that isomeric metallic nitrites of both types exist which are also *tautomeric* in a marked degree.

A great deal of most interesting work has also been carried out with the apparently dihydroxylic sulphurous acid and sulphites,  $\text{H}_2\text{SO}_3$  and  $\text{R}_2\text{SO}_3$ . Sulphurous acid, or rather its salts, may obviously be represented by either of the following formulæ,

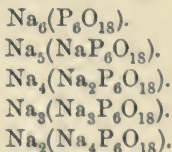


Michaelis (*Annalen*, 1892, 270, 108) considers sulphurous acid to be an aldehydic acid, and gives preference to the second formula, whilst Divers not only arrives at essentially the same conclusion in the course of his important researches, but does not consider that there is evidence for the existence of the dihydroxylic compound or its salts. If the second or sulphonic formula be correct, then two isomeric compounds of the formula  $\text{KNaSO}_3$  should exist, and Schwicker has obtained them (*Ber.*, 1889, 22, 1728; also Röhrig, *J. pr. Chem.*, 1888, [ii], 37, 217). The compound  $\text{Na}\cdot\text{SO}_2\cdot\text{OK}$  was produced by neutralising  $\text{Na}\cdot\text{SO}_2\cdot\text{OH}$  with potassium carbonate, and  $\text{K}\cdot\text{SO}_2\cdot\text{ONa}$  by neutralising  $\text{K}\cdot\text{SO}_2\cdot\text{OH}$  with sodium carbonate. The former, when treated with ethyl iodide at  $140^\circ$ , afforded the compound  $(\text{Et}\cdot\text{SO}_2\cdot\text{OK})_4\text{NaI}$ , and the second salt, by very similar treatment, gave  $(\text{Et}\cdot\text{SO}_2\cdot\text{ONa})_4\text{KI}$ . The proof of the isomerism of the two purely inorganic salts is therefore complete, and establishes their sulphonic formulæ and also of the



acid from which they are derived, but obviously does not affect the question of the existence of the form  $\text{SO}(\text{OR})_2$ . There is, however, independent evidence of the existence of such substances, as the true ester,  $\text{SO}(\text{OEt})_2$ , which boils at  $161^\circ$ , is completely saponified by alkalis, and the resulting sulphate seems to be symmetrical. The sulphonate,  $\text{Et}\cdot\text{SO}_2\cdot\text{OEt}$ , boils at  $213^\circ$  and is only partially saponified by alkalis. It is evident, however, that there is need for closer investigation of metallic sulphites with a view to the distinction of symmetrical compounds from those of sulphonic structure. Isomerism has also been observed between thiosulphates and the salts of some of the thionic acids.

As might be anticipated, the acids of phosphorus, owing to the high valence of the element, afford numerous examples of isomerism, as well as polymerism. Phosphorous acid, according to Zimmermann (*Ber.*, 1874, 7, 655) and Geuther (*Jena Zeitschrift*, [ii], 3), is  $\text{P}(\text{OH})_3$ ; on the other hand, Michaelis (*Annalen*, 1892, 270, 180) considers that the constitution of the acid is  $\text{H}\cdot\text{PO}(\text{OH})_2$ . Either two distinct isomeric phosphorous acids exist, or this is also a case of tautomerism, in any event requiring further investigation. Hypophosphates and hypophosphites are also said to exhibit isomerism. But the most interesting isomerides are those described by Tammann (*Zeit. physikal. Chem.*, 1890, 6, 122) in his researches on metaphosphates, and are of special interest because physical methods have largely aided in their recognition. From the study of the electrical conductivity and freezing points of solutions of the sodium and other salts, and by examining their modes of dissociation, he arrives at the conclusion that not only do  $\text{MPO}_3$ ,  $\text{M}_2\text{P}_2\text{O}_6$ ,  $\text{M}_3\text{P}_3\text{O}_9$ , and  $\text{M}_6\text{P}_6\text{O}_{18}$  exist [the salt  $\text{Ag}_5\text{NaP}_6\text{O}_{18}$  being an example of the last type], but also that five isomeric sodium salts of the last complex acid can be recognised through their mode of resolution into ions; their anions are included within brackets in the following table:



In a later paper (*J. pr. Chem.*, 1892, [ii], 45, 417), these conclusions seem to be confirmed from the purely chemical side, and even more complex salts are described.

In 1897, Sabanéeff (*Ber.*, 1897, 30, 285) pointed out the isomerism of hydroxylamine hypophosphite,  $\text{NH}_2\cdot\text{OH}, \text{H}_3\text{PO}_2$  and  $\text{NH}_4\text{H}_2\text{PO}_3$ , supposing this to be the first known case of such inorganic isomerism.

In a subsequent paper, he has described several other pairs of compounds, namely :

|                                       |                          |
|---------------------------------------|--------------------------|
| { Hydrazine phosphite .....           | $N_2H_4, H_3PO_3$ .      |
| { Ammonium hydrogen amidophosphate .  | $NH_4, H, NH_2PO_3$ .    |
| { Ammonium hydrogen hypophosphate...  | $(NH_4)_2, H_2P_2O_6$ .  |
| { Hydrazine hydrogen phosphite .....  | $N_2H_4, (H_3PO_3)_2$ .  |
| { Hydrazine hydrogen phosphate .....  | $N_2H_4, H_3PO_4$ .      |
| { Hydroxylamine amidohypophosphate... | $NH_2OH, NH_2PO(OH)_2$ . |
| { Hydrazine hypophosphate .....       | $N_2H_4, (H_2PO_3)_2$ .  |
| { Ammonium dimetaphosphate .....      | $(NH_4PO_3)_2$ .         |

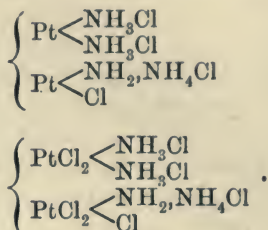
These are obviously cases of a different order of isomerism from those of Tammann previously noticed.

Salts of other polybasic acids, such as the borates, silicates, stannates, tungstates, molybdates, titanates, and the still more complex silico-tungstates, -molybdates, -titanates, &c., afford examples of isomerism which much need further investigation, but it is useless to add to those already given. It is highly improbable that carbon is the only element of its natural family which is capable of forming either simple or compound "rings" of atoms, either directly linked or with diverse atoms interposed. I have already hinted at a quasi-benzenoid character being recognisable in some silicates, but we may also look for it in elements of still higher valence. Tungsten and molybdenum we know with certainty to have the power of building up highly complex molecules by atomic linkage, but we do not know whether this is immediate or mediate through other elements whether in "chain" or as a ring. These compounds have hitherto been scarcely examined from this broader point of view, and would probably well repay further investigation.

Among the apparently simpler compounds of one of the elements just mentioned, namely, molybdenum, at least two isomeric oxychlorides seem to exist having the formula  $MoO_2Cl_2$ . One of these is stated to be obtained by directly heating molybdenum dioxide in chlorine, and represents molybdic anhydride,  $MoO_3$ , in which the place of one atom of oxygen has been taken by two of chlorine. The second is produced by breaking down by heat the higher oxychloride,  $Mo_2O_3Cl_2$ , in presence of air. This may be a polymeride,  $Mo_2O_4Cl_2$ , of the first compound formed with absorption of oxygen, but the nature of the isomerism in this case also remains to be determined.

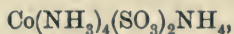
I now turn to a very different class of inorganic compounds in which isomerism has been frequently recognised, namely, that of the "metal ammonias." Platinum, chromium, cobalt, &c., are well known to afford complex compounds with ammonia, and among those derived

from platinum we can recognise at least two pairs of isomerides, namely :



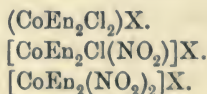
But the cobalt compounds of a similar order still more frequently exhibit isomerism between some praseo- and roseo-cobaltic bases, and Hofmann and Jenny (*Ber.*, 1901, 34, 3855) have recently recognised two isomerides in the cobalt-tetramine series which are *both* essentially praseo-compounds.

These are isomerides of



and cannot be regarded as merely polymorphous forms, as their reactions are different, and they are not mutually convertible by crystallisation.

Alfred Werner, to whose long-continued researches on the cobalt bases we owe a very large amount of information, has not only investigated several structural isomerides, but has recently recognised two groups of forms which are chiefly distinguished by *physical* properties (*Ber.*, 1901, 34, 1705). These, however, result from the replacement of ammonia in cobalt diamines by ethylene diamine. Representing the latter by En in the formulæ, the following have been produced :



Each of these exists in two forms, praseo-, or green, and "violeo-" compounds, and, since these isomerides do not show any difference in chemical structure, Werner considers that their widely different physical characters can best be accounted for by differences in the configuration of the molecules in space.

Many other illustrative cases of isomerism of either wholly or partly inorganic compounds might be cited, but probably a sufficient number has been noticed to justify the statement made at the outset, and to indicate that interesting studies of this order are by no means confined to carbon compounds.

There is another direction in which inorganic and organic substances



compare in a curious and interesting manner—I refer to catalytic actions. Bredig has brought together a number of examples under the somewhat sensational title of,

### *Inorganic Ferments.*

His inorganic ferments are generally the metals, platinum, gold, silver, palladium, iridium, mercury, &c., in colloidal metallic “solutions,” and he seeks to trace analogies between the chemical changes which they can determine and solutions of colloidal organic ferments, chiefly of the enzyme class (“Anorganische Fermente,” Dr. Georg Bredig, Engelmann, Leipzig).

The metallic solutions in question are most easily prepared by forming an electric arc under water between tolerably thick poles of the metal, platinum, for example. With a current of 12 to 14 amperes at 100 volts, the metal spatters so readily that a dark brown liquid is quickly obtained containing about 200 milligrams of platinum per litre. This passes through the finest filtering paper and may be kept for months without depositing metal. In the platinum, gold, silver, and other solutions obtained in this manner, the metals are present in the colloidal state, as they do not diffuse through an animal membrane, and therefore are in quasi-solution as “hydrosols,” to use Graham’s term for such liquids.

This state implies a much finer degree of division of a metal such as platinum than in platinum black or sponge, and consequently should be more effective in catalysis. Bredig reminds us that the metals, if only in fine powder, compare with ferments in bringing about the following changes :

(1) The oxidation of alcohol to acetic acid, in presence of air, by *mycoderma aceti* or by platinum black.

(2) The action of platinum, as well as some organic substances, on oxyhydrogen gas is shared by certain materials which are able to induce rotting through the presence of contained ferments.

(3) The decomposition of calcium formate into calcium carbonate, carbon dioxide, and hydrogen can be effected, not only by certain bacteria, but also by finely-divided iridium, rhodium, or ruthenium.

(4) The decomposition of dilute solutions of oxalic acid is brought about as well by metallic powders or sponge of platinum, silver, &c., as by moulds.

(5) Just as some kinds of bacteria are able to assimilate nitrogen, so can purified and moist spongy platinum, when exposed to air, yield traces of ammonium nitrite.

(6) Certain *confervæ* exert a reducing action on nitrates; the

latter are reduced also by hydrogen in presence of the finely-divided platinum metals.

(7) The accelerated oxidation of sulphur dioxide by air, in presence of platinum, has a kind of parallel in the oxidation of sulphur to sulphates by certain bacteria.

(8) Diastatic phenomena, such as the inversion of cane sugar, can also be accomplished under the influence of finely-divided metals.

(9) The blueing of tincture of guaiacum in presence of hydrogen peroxide is effected by organic ferments, red blood corpuscles, spongy platinum, finely-divided gold, silver, &c.

(10) Hydrogen peroxide is catalysed into water and oxygen by gold, silver, platinum, iridium, just as by blood fibrin, and, similarly, by many colloidal organic ferments, for example, diastase, emulsin, myrosin, yeast, pepsin, &c.

In these cases, the organic catalytic agent is a colloidal ferment, precipitable by ammonium sulphate, and very minute quantities of enzyme are able to decompose relatively very large amounts of hydrogen peroxide; this power is often lost, either by heating or by the addition of small quantities of certain materials. Blood corpuscles, the lymph of small-pox, pus, and certain toxins also decompose hydrogen peroxide, the power being destroyed by heating; it is temporarily lost under the influence of minute traces of hydrocyanic acid, but the ferments recover after exposure to air for some time.

The author finds that colloidal solutions of platinum, containing at most 1 milligram atom of metal per litre of water, behave in exactly the same way towards hydrogen peroxide and other substances as spongy platinum. Thus, iodised starch paste, containing sulphuric acid and exposed to air, becomes blue on the addition of the colloidal solution; guaiacum tincture, with or without hydrogen peroxide, turns blue; dilute ammonia is oxidised more rapidly in presence of permanganate; chloric acid or hydrogen peroxide more rapidly bleach indigo; hypochlorites are decomposed; chromous chloride, according to Ostwald, evolves hydrogen; a 10 per cent. solution of a nitrite, through which hydrogen is led, becomes alkaline. Hence the colloidal platinum solution exhibits to a marked degree the same activities as a ferment, and, although inorganic, presents many points of analogy with the organic enzymes, which are colloidal substances also.

Experiments were conducted by Bredig as to the proportions of hydrosol necessary to effect catalysis of hydrogen peroxide; as to the velocity of its decomposition; the influence of concentration of the hydrosol; the influence of electrolytes (acid, alkali, &c.); and the



influence of temperature; and the following interesting results were obtained.

Colloidal platinum was shown to perceptibly hasten the decompositions when the proportion of metal was 1 milligram atom in 70 thousand litres of water, and gold acted in the same way when similarly diluted with one thousand litres.

For a given proportion of gold or platinum colloid, the velocity of action rises to a maximum with increase of alkali, and thence diminishes until, in presence of alkali at normal strength, it falls below that in pure water. This behaviour presents a striking analogy to that observed by Jacobsen with hydrogen peroxide and organic ferments; for example, emulsin, or the enzymes of malt and pancreas; a similar behaviour has been observed by O'Sullivan and Thompson in the action of invertin on sugar, in contact with increasing amounts of sulphuric acid. It is also found that by increasing the proportion of hydrosol, the rate of catalysis accelerates in more than the corresponding ratio.

Electrolytes modify the colloidal condition, and hence affect the activity of the dissolved metal; the same is true for organic ferments.

The speed of catalysis increases with rise of temperature, so long as the rate of change of the colloid is slower than that of the decomposition which it causes. Eventually, however, the heating changes the colloid, especially in presence of electrolytes, and thereby rapidly diminishes its activity, it follows that, just as in the case of ordinary ferments, there exists a kind of *optimum* temperature. This requires that the duration of an experiment at any given temperature should be prolonged sufficiently to allow the heating to exert its full effect on the colloid.

The analogy between these inorganic colloids on the one hand, and the organic enzymes, or the blood, on the other, is surprisingly marked in respect of the way in which their activity becomes inhibited, by the presence of certain substances. Thus, the platinum hydrosol is paralysed so far as its catalytic power is concerned, and ceases to have any material effect on hydrogen peroxide, or to produce the blue colour with tincture of guaiacum, when mixed with 0·0000001 gram-molecule of iodine, or hydrogen sulphide, per litre, and half that proportion of hydrocyanic acid or cyanogen iodide. Expressed in the same units, this "poisoning" is accomplished by the following additions per litre: of  $\text{HgCl}_2$ , 0·000001; of  $\text{Br}_2$  or  $\text{NH}_2\cdot\text{OH}$ , 0·00004; of  $\text{C}_6\text{H}_5\text{NH}_2$ , 0·00018; of  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{PH}_3$  or  $\text{HCl}$ , 0·0002 to 0·0003; of  $\text{H}_2\text{C}_2\text{O}_4$  or  $\text{Na}_2\text{SO}_3$ , 0·001 to 0·002; and of  $\text{HgCy}_2$ , 0·0048. In addition, carbonic oxide, arsenic trihydride, carbon disulphide, and arsenious acid showed marked capacity for inhibition, while potassium chlorate,



sulphuric and nitric acids, alcohol, ether, &c., are practically inoperative. It was noted that a platinum hydrosol which had been "poisoned" by carbonic oxide, and subsequently "recovered," was more active than the original hydrosol. These phenomena may, perhaps, be due to (1) absorption, whereby at first the metallic surface becomes covered, and therefore rendered inactive, and (2) subsequent combustion of the carbon monoxide, the metal now being left with a cleaner surface than it possessed before coming into contact with the monoxide. Either explanation implies that the "hydrosol" includes the metal in an exceptional state of extension; but it is by no means certain that the metal is merely in that condition, and is not present in feeble combination with the elements of water.

This is merely an outline of a portion of a very interesting thesis which seems to be but little known in this country; but my chief reason for referring to this work is that it carries on the illustrations which may be cited in support of the proposition with which I began, namely, that the broader study of inorganic chemistry, especially in the light of our knowledge of the organic division of the science, is well worthy of much greater attention than it has hitherto received.

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#### OBITUARY NOTICES.

GEORGE GRIFFITH, born in 1833, was son of the vicar of Llan-gunnor, Carmarthenshire, and at an early age attracted the attention of Bishop Thirlwall, who undertook his education, and by whom he was sent to Grove House School in St. David's. In due time, Griffith matriculated at Jesus College, Oxford, where, after taking honours in both Classical and Mathematical Moderations, he was placed alone in the First Class of the Final Honour School of Natural Science in 1856. He was elected Fellow of our Society in 1859.

For the next eleven years, Oxford was his home. He intended to enter the medical profession, and for some time studied at the Radcliffe Infirmary, but gradually, as the claims of pure science became more pressing, the medical project faded out. During these years, we find him lecturing on science and mathematics for Jesus College, teaching in Magdalen College School, and delivering a weekly science lecture at Winchester College. He also held the post of Assistant to the Professor of Natural Philosophy (Professor Walker), and was subsequently appointed Deputy Professor.

In 1867, he left Oxford in response to a call from the headmaster of Harrow School, and from this time until his death made Harrow his home.

Griffith's task was no light one, Systematic science teaching in

schools was at that time unknown in England. He had to institute and organise a new branch of study, without laboratory accommodation and without apparatus, in the face of the indifference of most of his colleagues and the undisguised antipathy of the boys. For twenty-six years, he laboured at Harrow, during which time the change of attitude of both masters and boys towards scientific study was so marked that, to his younger colleagues, the stories of his early struggles seemed well-nigh incredible.

At first, Griffith had sole charge of the science teaching, and undertook with enthusiasm the teaching of chemistry, physics, geology, and biology, but after the completion of the school laboratories in 1874, a colleague was appointed to take over the chemical department, and from this time forth Griffith devoted himself almost exclusively to physics.

In 1893, he retired from his mastership, but continued to reside in Harrow.

Outside of Harrovian circles, it is as Assistant General Secretary of the British Association that Griffith is best known. His connection with the British Association began in 1860, when he acted as local secretary for the Oxford meeting. From 1862 to 1878, he held the post of Assistant General Secretary, but was compelled to resign owing to the pressure of school work. In 1881, he was prevailed upon to undertake the duties during a vacancy, and in 1890 was reappointed, and carried on the duties of his office until the day—almost the hour—of his death.

In his later years, he was greatly occupied with the International Catalogue of Scientific Literature, a work for which he was singularly well fitted by his wide scientific and linguistic knowledge.

On May 7th, 1902, as he was returning by rail to Harrow from his work in London, he was seized with an attack which ended fatally before he could be conveyed to his home.

"Dry light" was the key-note of Griffith's character. Fastidiously exact in thought and diction, he was ever ready to do battle in the cause of accuracy against confused thinking and slipshod speech. This attitude of mind, combined with his encyclopædic knowledge, made him a bracing talker, and one invariably left his company with a sense of knowledge gained and haziness dispelled.

In his work for the British Association, Griffith showed another side of his nature. Here he was the shrewd man of business, tactful, firm, resourceful, of untiring industry and endless patience, with an underlying fund of humour which was of no slight help among the difficulties of his office.

B. P. LASCELLES.



JOHN JAMES HUMMEL.—By the death of Professor Hummel, the art of dyeing has lost one of its most brilliant exponents, for he was the pioneer teacher of this subject, as well as an arduous worker and scientific investigator. The experience acquired in the works as manager, and also as practical chemist, combined with his training in the technical school at Zurich under Stadelcr and Wislicenus, qualified him for the work of initiating the Dyeing Department of the Yorkshire College, with which his name will always be associated.

John James Hummel was of Lancashire birth, being born in Clitheroe, but his father was a native of Switzerland and a technical chemist, who had occupied positions of responsibility in dyeing and printing works at Elbeuf, Paris, and Rouen, and subsequently in the printing works of James Thomson, F.R.S., of Clitheroe. The influence of Mr. Thomson brought him into touch with many eminent scientific men, and, amongst others, Frederick Steiner, John Mercer, Walter Crum, Daniel and Camille Koechlin. It was only natural that Mr. Hummel should inherit ability for scientific pursuits, and that although for a time he entered business, he should manifest a decided taste for some branch of technical chemistry.

After training under Mr. Knecht, B.Sc., and a short term in a Manchester office, he studied for three years in the Zurich Polytechnic, where he obtained his diploma. He subsequently adopted the profession of his father by entering a calico print works as chemical adviser. Dr. Grace Calvert, F.R.S., offered him an assistantship in the Manchester Royal Institution Laboratory, but this he declined, accepting the post of chemist in the print works of Messrs. James Black & Co., near Glasgow. His faculty for teaching and his interest in technical education were first exercised while with this firm, for he formed a class in chemical technology, bearing specially on dyeing and printing. The instruction was imparted gratuitously, and not a few of the young men who attended the course attribute their success in life to this training. Later, he was manager, first in a print works in Lancashire, and then for a firm of woollen yarn dyers in Scotland.

In 1879, the Clothworkers' Company of the City of London extended their Departments at the Yorkshire College by establishing a School of Dyeing, and Mr. Hummel, early in 1880, was appointed to the Professorship of the new Department. His success as a teacher was soon recognised, and in 1885, well-equipped buildings with suitable lecture room, museum, experimental dyehouse, and laboratories were erected. Since that time; students have been trained under Professor Hummel from all parts of the United Kingdom, and also from the Continent, America, Canada, Japan, and other countries.

Some four years ago, Professor Hummel advocated the importance of scientific research in the chemistry of dyeing, and, as a result, the



research laboratory and other extensions of the dyeing department were equipped and formally opened in May, 1900. These also comprise pattern and practical dyehouses, so that the equipment which Professor Hummel designed and installed with a mastery of detail is unsurpassed by that of any other school of dyeing in the world, and deals in the fullest degree with the teaching of this subject, both in its purely scientific and practical aspects.

The commencement of this work and of the woollen and worsted yarn spinning branches of the textile industries department have produced an educational unity between the Clothworkers' departments which has rendered practicable the teaching of the science and practice of the manufacture of all kinds of woollen, worsted, and mixed fabrics to an extent not yet possible in any Continental or American school. The experiments conducted are of such a nature as to show the influence of the dyeing processes upon the nature of the material, the spun yarn, and the woven fabric. It was the desire of Professor Hummel to perform the practical dyeing of materials, yarns, and cloth with the method and business accuracy characteristic of actual works.

As a lecturer and teacher of experimental science, the late Professor possessed natural and trained ability. Fluent and clear, and competent to expound every detail of the subject under discussion, his style was methodical, analytical, and concise. In his lectures, he had recourse to his experience in the works, and recognising the value of illustration and experiment he made ample use of diagrams, lantern slides, and specimens. Those who have studied under him have many incidents by which to recall his kindness, willingness to help in a difficulty, and sympathetic encouragement rendered to the earnest seekers after knowledge.

Mr. Hummel has made several valuable contributions to literature on the science and technology of dyeing. His principal work, "The Dyeing of Textile Fabrics," has been translated into German, Italian, and Japanese, and his articles on dyeing in the *Encyclopædia Britannica* and in various scientific and technical journals are well known to the dyeing industry. In recent years, his energies had been so absorbed with the new buildings that his literary activities had to be curtailed, but there is reason to believe that he was gleaning information and making experimental research which would have ultimately been published.

Those who knew Professor Hummel intimately can never readily forget his uniform thoughtfulness, true sympathy, and friendship. He was in every sense devoted to the task with which his life was so fully associated, but this did not prevent him from manifesting enthusiasm in the solution of the difficulties of others. He was highly

esteemed by his colleagues, by the textile and dyeing committees, and the Clothworkers' Company. A sincere and true man, he was faithful to duty, and lived for the high purpose of extending scientific knowledge and for the exercise of influences which would better humanity. In the Dyeing Department of the Yorkshire College, which his endeavour has organised, there exists a memorial of industry and of lasting service rendered to the science and art of dyeing.

R. U. HUMMEL.

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SIR WILLIAM CHANDLER ROBERTS-AUSTEN was born in March, 1843. His father, Mr. George Roberts, was of Welsh descent, whilst he was connected on his mother's side with the Kentish families of Chandler and Austen. He assumed the name of Austen in 1885 at the request of his uncle, Major Austen, J.P., of Haffenden and Camborne, in Kent. From 1861 to 1865, he studied at the Royal School of Mines, taking the Associateship in Metallurgy in the latter year. Shortly afterwards, he entered the Mint, and continued his connection with it during the whole of the remaining thirty-seven years of his life. He acted at first as private assistant to Professor Graham, then Master of the Mint, and was employed on the researches in physical chemistry, which continued to occupy Graham until his death in 1869. In 1870, Sir William Roberts-Austen was appointed Chemist of the Mint on the creation of that post, and in 1871, on the abolition of the non-resident assayerships, the Assay Office for the verification of the standard of fineness of coinage bars and of finished coin was re-established, after having been in abeyance since 1851, and was placed under his direction. In 1882, he was also entrusted with the duties formerly performed by the King's Assay Master, including the trial of the diets of the offices for hall-marking gold and silver wares at Birmingham, Sheffield, and Chester. During the time that he held office he became responsible for the standard fineness of about £150,000,000 of gold coin, over £30,000,000 of imperial silver coin, and about £10,000,000 of bronze and Colonial silver coin. In June, 1902, on the death of Sir Horace Seymour, the late Deputy Master of the Mint, Sir William Roberts-Austen was appointed Deputy Master *ad interim*, and, in spite of the progress of his malady, from which he had suffered for some months, he continued to direct the operations of the Mint until a few days before his death, which occurred on November 22nd.

The scientific researches of Sir William Roberts-Austen were mainly directed to the investigation of the properties of metals and alloys, and during the last few years he has been one of the most



distinguished of the band of workers by whom the new branch of science, "Metallography," has been developed.

The first problem of importance which he attacked was the cause of the well-known segregation in the alloys of silver and copper, by which the two metals become unevenly distributed in solid ingots. The paper describing his results was published in 1875. For the next few years he occupied himself in determining a number of the physical constants of metals, and in attempts to improve the methods of assaying, applying the spectroscope, in conjunction with Sir J. Norman Lockyer, and using the induction balance, in collaboration with Prof. Hughes. In 1888, he published the results of an elaborate research on the effects of traces of impurities on the mechanical properties of pure metals, and succeeded in showing that the effects were generally proportional to the atomic volumes of the elements, and in this way connected with the Periodic Law. The direct result of this research, and of his contributions to the study of the hardening and tempering of steel, was the establishment of the Alloys Research Committee of the Mechanical Engineers. This Committee supplied the financial support necessary for the pursuit of such work, and the results were in the highest degree encouraging to those who were so generously endowing science. Five successive Reports were issued embodying the work done by Sir William Roberts-Austen, and a final report, unfinished, awaits publication. The first, submitted in 1891, contained a description of the recording pyrometer, an improved form of the Le Chatelier pyrometer, by which the temperature of furnaces or masses of metal and the exact time at which each change in temperature occurs are recorded in the form of a curve traced on a moving photographic plate. This instrument has proved to be a powerful weapon of research, and is also widely used in the industries. In the second report, issued in 1893, the effects of arsenic, antimony, and bismuth on copper were discussed, and the thermal behaviour of chromium-steel was described. The third report dealt with electric welding and with the alloys of iron and aluminium. The fourth report, of 1897, contained the results of a beautiful series of experiments on the diffusion of metals in each other which had formed the material of the Bakerian lecture of the Royal Society delivered in 1896. The lead-tin, copper-zinc, and copper-lead series of alloys were also discussed. Finally, in the report issued in 1899, carburised iron was dealt with, and the treatment of steel rails considered from various points of view. The sixth report, not yet issued, is concerned with the thermal treatment of steel and its effects on the microstructure and other physical properties of the metal, and an appendix on the microscopic structure of the alloys of copper and tin has already been presented to the Institution of Mechanical Engineers.



All these reports have proved to be of the highest scientific and practical value.

Among other researches, the results of which were published during this period, there may be mentioned those on the carburisation of iron by the diamond; on the action of projectiles and of explosives on gun tubes; on the diffusion of carbon in iron; on the diffusion of gold in solid lead; and on the gold-aluminium series of alloys. In the course of the last-named work, he discovered the purple alloy,  $\text{AuAl}_2$ , which is associated with his name.

Sir William Roberts-Austen's activities were by no means confined to his scientific researches and to his ordinary official duties. In 1880, he succeeded Dr. Percy as Professor of Metallurgy at the Royal School of Mines, and alike in his Introductory Lecture and in his subsequent thoughtfully framed and brilliantly delivered courses of lectures he showed how much he had the interests of his old school at heart. The students whom he has trained are grateful to him for the stimulating influence of his teaching and for the many proofs he gave of the kindly feeling with which he regarded them. His *Introduction to the Study of Metallurgy*, now in its fifth edition, embodies the substance of his preliminary course of lectures, and remains as a token of the importance he attached to the formation of a substantial foundation of scientific principles on which to base the mass of details required by metallurgists in their practical work.

As a public lecturer, Sir William Roberts-Austen was completely in his element. His five courses of Cantor Lectures on Metals and Alloys at the Society of Arts, his Friday evening discourses at the Royal Institution, his lectures at the British Association, and the James Forrest Lecture to the Civil Engineers, all copiously illustrated with remarkable experiments, testified to his marvellous powers of gaining the attention of an audience and of holding it interested and delighted to the end. His two Presidential addresses to the Iron and Steel Institute, in which the work of his predecessors and of the French metallurgists was eulogised, were scholarly in style and comprehensive in treatment. All his lectures and addresses were, indeed, finished works of art, on which he spent no small pains in the determination to make them as perfect in form as they were in subject matter.

Sir William Roberts-Austen served on several departmental and other committees. He was a member of the Executive Committee of the Inventions Exhibition in 1885, of the Council of the British Section of the Paris Exhibition in 1889, and of the Royal Commission for the Chicago Exhibition in 1893. He served as Chairman of the Inland Revenue and Customs Laboratories Committee in 1893, and a member of the Periyar Irrigation Committee in 1893, of the Board

of Trade Committee on the Deterioration of Steel Rails in 1896, and of the National Physical Laboratory Committee in 1897. During the last two years of his life, he was a member of the Explosives Committee of the Admiralty and War Office, and devoted much time and thought to its service at a time when his arduous labours in other directions were beginning to tell on his strength, and his failing health seemed to counsel him to seek some repose.

He was made a C.B. in 1890, and a K.C.B. in 1899. He was also a Chevalier of the *Légion d'Honneur*, and received the degree of Doctor from Durham and Victoria Universities. He was elected into the Royal Society in 1875. He became a Fellow of the Chemical Society in 1866, served on the Council from 1879 to 1881, and was a Vice-President from 1895 to 1898. He was also a Vice-President of the Physical Society, of which he was one of the founders, President of the Iron and Steel Institute from 1899 to 1900, General Secretary of the British Association from 1897 to 1902, Vice-President of the Institution of Mining and Metallurgy, Member of Council of the Society of Arts, and Honorary Member of the Institution of Civil Engineers, of the *Société des Ingénieurs Civils de France*, of the Institution of Mechanical Engineers, and of the American Institution of Mining Engineers.

He possessed a charm of manner and a knowledge of men which ensured his popularity among a large circle of friends.

His kindly, considerate, and deeply religious nature made him an excellent neighbour at Chilworth, in Surrey, where he had built himself a beautiful cottage on a breezy heath. He was never tired of interesting himself in the welfare of the poorer inhabitants of the district. He was chiefly responsible for the erection of a chapel of ease in the hamlet of Chilworth, where previously there had been no place of worship, and, acting under a license from the Bishop of Winchester, frequently officiated at the services himself. He personally undertook the direction of the decoration of the interior of the chapel, and the beautiful mural paintings with which it is embellished remain as a monument to his artistic perceptions and generous instincts.

T. K. ROSE.

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## LXVII.—*The Absorption Spectra of Nitric Acid in Various States of Concentration.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

IN the communication entitled "The Absorption Spectra of Metallic Nitrates, Part II" (this vol., p. 221), attention was directed to the fact that nitric acid of sp. gr. 1.431 in a thickness of 2 mm. transmitted a longer spectrum than the same quantity of acid diluted to about 36 times its volume when examined in columns 100 mm. in length.

The experiments were varied and repeated, fresh measurements were made and controlled, but always with substantially the same results. The acid examined was taken from a full Winchester quart of the purest nitric acid specially prepared for use in gold and silver assays; it was colourless and free from nitrous and sulphuric acids. Any trace of chlorine it contained was less than 1 in 10 million parts of the acid. In applying the tests, quantities of 100 c.c. were suitably diluted and, when necessary, also neutralised with pure ammonia. A portion of the original acid which was concentrated by distillation with Nordhausen sulphuric acid yielded a distillate having a very pale yellow tinge, with a sp. gr. 1.490; this product was quite free from sulphuric acid and chlorine, but on diluting with water the small quantity of dissolved  $N_2O_4$  present yielded nitrous acid. The actual amount determined with *m*-phenylenediamine and a standard solution of nitrous acid prepared from silver nitrate was found to be equivalent to 5.7 parts of  $N_2O_4$  per 10,000 of nitric acid. To ascertain whether a thickness of 3 mm. of nitric acid of sp. gr. 1.490 contained sufficient nitric peroxide to affect the transmission of the ultra-violet rays, a quantity of this gas equivalent to that contained in the acid was dissolved in carbon tetrachloride and its spectrum photographed in a cell 3 mm. thick. It was found that the rays transmitted by nitric acid were not affected in the slightest degree by the solution of  $N_2O_4$  in carbon tetrachloride, since the  $N_2O_4$  caused feeble absorption between  $1/\lambda$  3300 and 3800; and nitric acid transmitted nothing beyond 3079.

The following is a tabulated statement of the spectra transmitted through 3 mm. of the liquid at various dilutions, containing 1.2 c.c. of the acid, and an additional table showing the effect of diluting 1.2 c.c. of the acid to 18 c.c. with distilled water, and examining it through a column of 50 mm. The specific gravities of the acids were accurately determined with Westphal's balance at 15°. The corresponding composition of each of the acids was taken from Lunge and Rey's tables. The diagram also shows at a glance the difference between the spectra transmitted by the strong and the diluted acids,



*Absorption Spectra of Nitric Acid.*

| Strong acid, 1.2 c.c., 3 mm. |                            |  |                           |  | Dilute acid, 18 c.c., 15 mm.               |                           |                           |  |
|------------------------------|----------------------------|--|---------------------------|--|--|---------------------------|---------------------------|--|
| Sp. gr. at 15°.              | HNO <sub>3</sub> per cent. | Ratio HNO <sub>3</sub> : H <sub>2</sub> O. | Spectrum continuous       | Extension weak, lines at                             | Ratio HNO <sub>3</sub> : H <sub>2</sub> O. | Spectrum continuous       | Weak extension            |  |
| 1.490                        | 89.60                      | 3 : 1                                      | <sup>1/λ</sup><br>to 2644 | <sup>1/λ</sup><br>3685, 2718 to 2743<br>3105 to 3150 | —  | <sup>1/λ</sup><br>to 2939 | <sup>1/λ</sup><br>to 2991 | Readings on other plates.<br>Plate D<br>" C<br>" B |
| 1.432                        | 72.57                      | 3 : 4                                      | " 3079                    | —  | 1 : 36                                     | " 2983                    | " 2991                    |  |
| 1.420                        | 69.80                      | 2 : 3                                      | " 3079                    | —  | 1 : 43                                     | " 3006                    | " 3043                    |  |
| 1.397                        | 63.63                      | 1 : 2                                      | " 3079                    | —  | 1 : 57                                     | " 2983                    | " 3006                    |  |
| 1.339                        | 53.93                      | 1 : 3                                      | " 3079                    | —  | 1 : 71                                     | " 2983                    | " 3006                    |  |
| 1.263                        | 41.18                      | 1 : 5                                      | " 3079                    | —  | 1 : 92                                     | " 3002                    | —                         |  |
| 1.207                        | 33.33                      | 1 : 7                                      | " 3079                    | —  | 1 : 123                                    | " 3002                    | —                         |  |
| 1.127                        | 20.31                      | 1 : 14                                     | " 3079                    | to 3083  | 1 : 232                                    | " 3072                    | —                         |  |
| 1.432                        | —                          | 3 : 4                                      | " 3079                    | —  | 1 : 36                                     | " 2946                    | —                         |  |
| 1.420                        | —                          | 2 : 3                                      | " 3079                    | —  | 1 : 43                                     | " 2939                    | " 2991                    |  |
| 1.339                        | —                          | 1 : 3                                      | " 3079                    | —  | 1 : 71                                     | " 3006                    | —                         |  |
| 1.127                        | —                          | 1 : 14                                     | " 3079                    | —  | 1 : 232                                    | " 3072                    | —                         |  |

\* Reading <sup>1/λ</sup> 3086 on plate C on two occasions, but the spectrum practically ends at the same line, <sup>1/λ</sup> 3079, on all these plates.

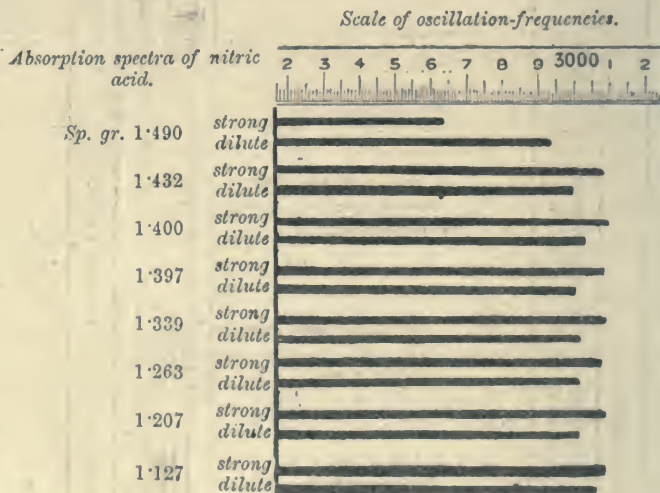
*Nitric Acid Diluted and Examined through a Thickness of 3 mm.*

| Ratio HNO <sub>3</sub> : H <sub>2</sub> O. | Spectrum continuous       | Extension weak            | Absorption band.               | Rays transmitted.           |
|--|---------------------------|---------------------------|--------------------------------|-----------------------------|
| 1 : 21                                     | <sup>1/λ</sup><br>to 3079 | <sup>1/λ</sup><br>to 3157 | <sup>1/λ</sup><br>3157 to 3662 | <sup>1/λ</sup><br>3662—3947 |
| 1 : 28                                     | " 3114                    | " 3157                    | 3157 " 3537                    | 3537—3947                   |
| 1 : 35                                     | " 3114                    | " 3157                    | 3157 " 3507                    | 3507—3947                   |
| 1 : 42                                     | " 3114                    | " 3193                    | 3193 " 3507                    | 3507—3980                   |
| 1 : 49                                     | " 3157                    | " 3980                    | —                              | to 3980                     |

through 3 mm. and 50 mm. respectively, the actual quantity of nitric acid being the same in each experiment. The dilution is effected with 15 volumes of water in each case :

*Nitric Acid Diluted and Examined through a Thickness of 50 mm.*

| Ratio<br>$\text{HNO}_3 : \text{H}_2\text{O}$ . | Spectrum continuous            | Extension weak                 |
|--|--------------------------------|--------------------------------|
| 1 : 21   | $\frac{1}{\lambda}$<br>to 2939 | $\frac{1}{\lambda}$<br>to 2983 |
| 1 : 28   | „ 2939                         | „ 2983                         |
| 1 : 35   | „ 2939                         | „ 2983                         |
| 1 : 42   | „ 2933                         | —                              |
| 1 : 49   | „ 2983                         | „ 3002                         |



It will be observed that there are marked changes in the spectra photographed through 3 mm. of acid when the ratio of  $\text{HNO}_3 : \text{H}_2\text{O}$  is as 3 : 1, 3 : 4, 2 : 3, and 1 : 2, but in solutions more dilute than that indicated by the last of these ratios, the spectrum transmitted by 3 mm. of the strong acid is practically the same for acids of different specific gravities, and in the dilute solutions of these acids a shorter spectrum is transmitted until the ratio 1 : 14 is attained. Thereabouts, the strong and the dilute acids transmit almost the same spectrum, but beyond this point a thickness of 3 mm. of the dilute acid shows a more regular variation and exhibits a very definite absorption band. The general absorption, in nearly every case, is cut off with remarkable abruptness, that is to say, without any gradual weakening of the

spectrum. Acid of higher specific gravity than 1.490 has not been examined, because there are practical difficulties to contend against, which up to the present have not been satisfactorily overcome. As Veley and Manley have shown (*Phil. Trans.*, 1898, 191, 365), a pure acid of the formula  $\text{HNO}_3$  is difficult to obtain; it absorbs water with the avidity of oil of vitriol, besides which, as is well known, it is decomposed by heat and light. It exudes from the quartz cells during examination, and from the corrosive nature of both the liquid and its vapour it is not easily manipulated. Near to those points where Veley and Manley (*Proc. Roy. Soc.*, 1901, 69, 86) noticed very marked physical differences in solutions of nitric acid, it is found that the changes in the absorption spectra occur where the ratio of acid to water is as 3 : 1, 3 : 4, and as 2 : 3.

The greatest change on dilution is seen with the solution of sp. gr. 1.490 containing 89.6 per cent. acid (3 mols.  $\text{HNO}_3$  : 1 mol.  $\text{H}_2\text{O}$ ). Here the spectrum is the shortest and dilution lengthens it. With the next acid of sp. gr. 1.432 or 72.57 per cent. (3 mols.  $\text{HNO}_3$  : 4 mols.  $\text{H}_2\text{O}$ ), the transmitted spectrum is longer than that of any of the six succeeding weaker acids, and the effect of dilution is strikingly the reverse of that in the preceding case, since it shortens the spectrum. With acid of sp. gr. 1.420 or 69.80 per cent. (2 mols.  $\text{HNO}_3$  : 3 mols.  $\text{H}_2\text{O}$ ) a slightly shorter spectrum is transmitted, which is still further shortened by dilution. From this point, onwards, until the acid is diluted with 14 molecules of water, the sp. gr. being 1.127 (20.31 per cent.  $\text{HNO}_3$ ), the spectra transmitted are practically the same, but the diluted acids transmit spectra which, although shorter, increase in length. The increase is not gradual, and, finally, the acid with 14 molecules of water transmits through 3 mm. almost the same length of spectrum as that with 232 molecules through 50 mm. There cannot be a doubt but that dilution alters the constitution of nitric acid of sp. gr. 1.432, and that the effect of diluting silver nitrate solution is the opposite of that observed with nitric acid (*Trans.*, 1902, 81, 572). With many salts there is no difference in their spectra, whether the same quantity of material is observed in a small thickness of a strong solution or in a great thickness of a dilute one. It is obvious that the water does not act simply as a diluent, for if it did dilution would cause an increase in length of the transmitted spectra, which would be proportional to the quantity of water present. There is evidently some chemical action between the water and the acid, but this action with acid of sp. gr. 1.490 is different from that with acid of sp. gr. 1.432 or any less concentrated solution. The remarkable extent to which the spectrum is absorbed by nitric acid of sp. gr. 1.490 is another instance of the general effect observed in a large number of cases where the



quantity of oxygen in the molecule of a substance is increased, or where a substance is polymerised. In other words, the spectrum affords evidence that in all probability the acid is more or less of the nature of  $n(\text{HNO}_3)$ , or of  $\text{N}_2\text{O}_5, \text{H}_2\text{O}$ . There is at present no evidence to show whether the acid might be more correctly represented as a mixture of molecules thus:  $\text{H}_2\text{N}_2\text{O}_6 + \text{HNO}_3 + \text{H}_2\text{O}$ , or as one compound  $\text{H}_3\text{N}_3\text{O}_9, \text{H}_2\text{O}$ .

Dilution of the acids, which range from sp. gr. 1.432 to 1.127 or within the limits  $3\text{HNO}_3 : 4\text{H}_2\text{O} \text{---} \text{HNO}_3 : 14\text{H}_2\text{O}$ , causes apparently an increase of weight in the molecule, such as would occur with the formation of hydrates if no other change were possible, and this is in accordance with the evidence afforded by Veley and Manley's examination of other physical properties of these dilute acids, namely, (1) the electric conductivity, (2) electric temperature coefficients, (3) the refractive indices, and (4) contraction of volume on dilution. It may be worth while recording that the five acids of greatest concentration, commencing with that containing 89.6 per cent. of  $\text{HNO}_3$ , may be formulated by assuming the existence of orthonitric acid and several hydrates, thus: (1)  $\text{H}_2\text{N}_2\text{O}_6, \text{H}_3\text{NO}_4$ , (2)  $3\text{H}_3\text{NO}_4, \text{H}_2\text{O}$ , (3)  $2\text{H}_3\text{NO}_4, \text{H}_2\text{O}$ , (4)  $\text{H}_3\text{NO}_4, \text{H}_2\text{O}$ , (5)  $\text{H}_3\text{NO}_4, 2\text{H}_2\text{O}$ .

### *Some Chemical Properties of Strong Nitric Acid.*

In the formulæ suggested, I have assumed the existence of orthonitric acid,  $\text{H}_3\text{NO}_4$ , firstly, because W. H. Perkin, sen., found the magnetic rotation of nitric acid containing 56.74 per cent. of  $\text{HNO}_3$  to be considerably less than that given by  $\text{HO} \cdot \text{NO}_2 + 2.67$  mols. of  $\text{H}_2\text{O}$ , and therefore the combination formed had a constitution in which there were not fewer than two hydroxyls; for this, the calculated rotation would be about 1.930. The actual number found, however, was 1.986. This might result from such a combination as  $\text{H}_3\text{NO}_4, 2\text{H}_2\text{O}$ .

The existence of  $(\text{HO})_3\text{N}:\text{O}$  is regarded by Perkin as not improbable, inasmuch as we have the analogous acid  $(\text{HO})_3\text{P}:\text{O}$ , and several nitrates corresponding thereto, as for instance,  $\text{Hg}'''\text{N}_2\text{O}_8$ ,  $\text{Cu}''\text{N}_2\text{O}_8$ , and  $\text{Pb}''\text{N}_2\text{O}_8$ . Nitrates of the alkali metals similar to the orthophosphates are, however, unknown (Trans., 1889, 55, 680; also 1893, 63, 57).

Secondly, Pickering isolated an acid in crystals with the composition  $\text{H}_3\text{NO}_4$ , containing 77.9 per cent. of  $\text{HNO}_3$ , whilst the theoretical number is 78.02 per cent.

The trihydrate, containing 53.85 per cent. of  $\text{HNO}_3$ , was also isolated, and gave, after two crystallisations, a substance containing

54.05 per cent. of  $\text{HNO}_3$ . This may be formulated as  $\text{H}_3\text{NO}_4 \cdot 2\text{H}_2\text{O}$  (Trans., 1893, 63, 486).

If the acid of sp. gr. 1.49 contains two differently constituted molecules, they might exhibit different chemical properties; and the electric conductivities measured by Veley and Manley (*Phil. Trans.*, 1898, 191, 365) support this view. For instance, the specific resistance  $\rho$  of nitric acid at  $15^\circ$  increases enormously and with great rapidity from an acid solution of 80 to one of 96 per cent.  $\text{HNO}_3$ , at which point a sudden reversal occurs. Below the inferior limit there is a slow increase of resistance from 33 per cent. up to about 70 per cent., from which point the augmentation is more rapid. At 78.02 per cent. the acid has the composition  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  or  $\text{H}_3\text{NO}_4$ .

Veley and Manley state that acid of 99.975 per cent. concentration has no action on several of those metals most easily attacked by dilute acids. It has, on the other hand, the highest possible efficiency in the two chemical effects of nitration, and oxidation of sulphur and sulphides. It has no action on finely powdered calcite or marble even if it is boiled with these substances.

The acid obtained by me of approximately 89.6 per cent. concentration may be regarded as a mixture of  $\text{H}_2\text{N}_2\text{O}_6$  with  $\text{H}_3\text{NO}_4$ . In such a case, oxides, carbonates, and metals might be expected to react with the  $\text{H}_3\text{NO}_4$  molecule, but not with the  $\text{H}_2\text{N}_2\text{O}_6$ , which corresponds with Veley and Manley's acid. In this mixture,  $\text{H}_2\text{N}_2\text{O}_6$  being inactive, would probably act as a diluent of the orthonitric acid,  $\text{H}_3\text{NO}_4$ .

To ascertain how far this might be correct, the following experiments were made: pieces of sodium carbonate, dehydrated by partial fusion, also magnesite, calcite, marble, strontianite, and witherite weighing from about 0.5 to 1.0 gram, were placed in beakers with 10 c.c. (about 14.9 gram) of the acid; the alkaline earth carbonates were apparently not acted on, and even after digesting for 50 hours no gas was seen to escape. The crystals of calcite alone appeared to be slightly dull, as if etched on the surface. A compact piece of an opaque variety of calcite, weighing 3.05 grams, after digestion in 10.57 grams of acid for 24 hours, weighed 2.95 grams, and had therefore lost 0.1 gram in weight, but clear, pale straw-yellow Iceland spar, weighing 1.5 grams, became quite colourless after digestion in 10.75 grams of acid for 24 hours, and had lost only 0.005 gram.

The sodium carbonate placed in this strong acid evolved a slight stream of minute bubbles for about two hours, after which the action ceased. After remaining in the acid for 50 hours the sodium carbonate was separated by decanting off the acid. The carbonate, when washed four times with absolute alcohol, was dried between

folds of blotting paper, and warmed to expel alcohol ; it weighed exactly 0.25 gram. It effervesced and dissolved in a few minutes in dilute acetic acid.

A piece of burnt lime kept in a desiccator, and weighing about 0.5 gram, was dropped into 10 c.c. of acid. It produced momentarily an ebullition and a slight red fume, but subsequently a piece weighing 0.17 gram remained undissolved for more than five days. The acid was then decanted, and the lime washed four times with absolute alcohol. When it had been dried, it was found to possess all the properties of caustic lime. In each experiment, the slightly yellow acid became quite colourless.

Potassium carbonate, heated to incipient fusion, was thrown into 10 c.c. of the acid ; it effervesced violently and evolved red fumes. To ascertain the nature of the reaction, 1.60 grams of the partially fused carbonate were placed in a stoppered cylinder with 2.75 grams of nitric acid solution ( $\approx 2.46$  grams  $\text{HNO}_3$ ) and left to digest for  $6\frac{1}{2}$  hours, when 80 c.c. of alcohol were added.

The alcohol was drained from the crystals in the cylinder, and titrated with  $N/10$  sodium hydroxide solution made from sodium.

The free acid found by titration was equivalent to 0.896 gram ; hence it is estimated that 1.56 grams were neutralised whilst theory requires 1.475 grams. A slight loss of acid had doubtless occurred by the rise of temperature and fuming of the acid during the escape of the carbon dioxide, hence we may conclude that the decomposition of the potassium carbonate was complete. The difference in the behaviour of the potassium and sodium carbonates is remarkable.

It seemed desirable to ascertain the extent to which calcite or marble would interact with acids of different concentrations, which, when judged by their spectra, might be considered to have a constitution differing from that of the 89.6 per cent. acid. Pieces of calcite, weighed and placed in stoppered cylinders, were mixed with weighed quantities of nitric acid, and left to digest for periods varying from 20 to 30 hours, or in one instance 50 hours. The undissolved calcite was weighed, and the residual nitric acid was determined by  $N/10$  sodium hydroxide solution. In experiments (3), (4), (5), and (6), the liquid became rather syrupy, but it remained clear and colourless after as much as possible of the calcite had been dissolved.

It was noticed that, in titrating the excess of acid in experiment (4), about 13 milligrams more of the acid had been neutralised than was the case with (3), (5), and (6), the reason probably being that the duration of the experiment was 20 hours longer. The quantity of acid not neutralised was in other cases 26 to 27 milligrams.

The following are the numerical details :



| <i>Nitric acid.</i>                                |                        | <i>Calcite.</i>        |                              |                      |                                       |
|--|------------------------|------------------------|------------------------------|----------------------|---------------------------------------|
| Approximate strength per cent. of $\text{HNO}_3$ . | Weight taken in grams. | Weight taken in grams. | Weight undissolved in grams. | Difference in grams. | Equivalent weight of $\text{HNO}_3$ . |
| 89.6   | (1) 1.43               | 1.55                   | 1.47                         | 0.08 *               | 0.10                                  |
|  | (2) 1.40               | 1.74                   | 1.70                         | 0.04                 | 0.05                                  |
| 72.57  | (3) 1.38               | 1.88                   | 1.07                         | 0.81                 | 1.02                                  |
|  | (4) 1.32               | 1.42                   | 0.65                         | 0.77                 | 0.97                                  |
| 69.8   | (5) 1.35               | 1.22                   | 0.47                         | 0.75                 | 0.945                                 |
|  | (6) 1.24               | 1.03                   | 0.35                         | 0.68                 | 0.856                                 |

\* The loss of weight of (1) was not entirely due to solution, but partly to the disintegration of the surface of the crystal; the separated particles could not be collected and weighed.

The calcite in (1) and (2) was left for 4 days in the acid. The surface of the crystals was etched, and the feebly straw-coloured substance was dissolved out of the crystals.

There was a considerable difference in the appearance of the several pieces of calcite after the removal of the acid; thus (1) and (2) were roughened on the surface, although the crystalline form was preserved and the edges of the crystals were sharp. In (1), minute crystalline fragments were detached, and it further appeared from the absence of any yellow tinge that something had been removed from the spaces between the planes of cleavage of the crystals.

In (3), (4), (5), and (6), on the other hand, there had been a real dissolution of the crystals, as shown by their rounded edges and the obliteration of the crystalline form.

When 3.26 grams of calcium oxide were added to 10.75 grams of the 89.6 per cent. nitric acid, the solution hissed and a fume of nitric acid arose, the temperature of the acid rising from  $20^\circ$  to  $59.5^\circ$ , but no further action took place. After 20 hours' digestion, the acid was poured off the lime; the latter, when washed three times with abundance of alcohol, and dried by gently heating, weighed 4.25 grams. After 24 hours in a desiccator, it was transferred to a beaker containing 250 c.c. of water tinted with neutral litmus solution. The liquid, which at first turned red, afterwards became blue; the lump of lime slaked and became a powder. Of the 3.26 grams of  $\text{CaO}$ , it was found that 2.48 grams were not neutralised by the acid. That which had been attacked amounted to 0.78 gram, corresponding with 1.755 grams of  $\text{HNO}_3$ . The increase in weight found agrees with that calculated for the formation of calcium nitrate from 0.78 gram of  $\text{CaO}$ .

Of real nitric acid, 10.75 grams of solution contained 9.632 grams, of which a little more than one-sixth had been neutralised. This appears to me conclusive evidence that the nitric acid contained two different molecules, one of which formed a calcium salt, whilst the other did not, for no less than 2.48 grams of calcium oxide remained in contact with a large excess of acid without any interaction occurring.

I propose to study the chemical properties of concentrated nitric acid more fully and precisely with a view to ascertaining its constitution.

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### LXVIII.—*The Action of Alkalis on Cinnamic Acid Dibromide and its Esters.*

By JOHN J. SUDBOROUGH and KENWORTHY J. THOMPSON.

THE reaction between cinnamic acid dibromide ( $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid) or its esters and alkalis has been studied by a number of investigators, and is the basis of the usual methods for the preparation of the  $\alpha$ -bromocinnamic acids.

Glaser (*Annalen*, 1867, 143, 325) obtained two monobromocinnamic acids by the action of alcoholic potash on a hot solution of  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid. The product, when neutralised with hydrochloric acid, was poured into water and evaporated to dryness; the solid residue was extracted with water and a small amount of tarry matter left undissolved. The two acids were then separated from the solution of their potassium salts by fractional precipitation with hydrochloric acid. The acid which was first precipitated, melted at 130—131°, whilst its isomeride melted at 120°; they were termed  $\alpha$ -bromocinnamic and  $\beta$ -bromocinnamic acids respectively, although the bromine in both acids was represented as occupying the  $\alpha$ -position with respect to the carboxylic group. The two acids are now usually known respectively as  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-cinnamic acids.

Barish (*J. pr. Chem.*, 1879, [ii], 20, 177) prepared these isomerides by the same method, and observed, in addition to the two acids, the formation of a small amount of oil, which was shown to be a bromocinnamene. The two acids were separated by Glaser's method, and it was found that the amount of the less fusible  $\alpha$ -bromo-acid was always far less than that of the  $\alpha$ -bromo*allo*-acid.

The production of the bromocinnamene was supposed to be due to the decomposition of one or both of the  $\alpha$ -bromo-acids, as the solution became strongly alkaline when evaporated, and the formation of the

oil was largely prevented by keeping the liquid faintly acid. Since the yield of the less fusible acid was always far below that of its isomeride, it was concluded that the oil was produced from the substance of higher melting point. The bromocinnamene formed was isomeric with the  $\alpha$ -bromocinnamene obtained from cinnamene dibromide, but identical with the bromocinnamene obtained by Glaser (*Annalen*, 1870, 154, 18, 168), and by Fittig and Binder (*ibid.*, 1879, 195, 142); the compound was therefore assumed to be a  $\beta$ -bromocinnamene,  $\text{CBrPh}:\text{CH}_2$ , and hence the acid melting at  $131^\circ$  would be a  $\beta$ -bromocinnamic acid,  $\text{CBrPh}:\text{CH}\cdot\text{CO}_2\text{H}$ , whilst its more fusible isomeride would have the formula  $\text{CHPh}:\text{CBr}\cdot\text{CO}_2\text{H}$ . The difference in melting points of the two acids and the inequality in reactivity of the halogen atoms in the different compounds were adduced in support of such formulæ for the two bromocinnamenes and the two bromo-acids.

Plöchl (*Ber.*, 1882, 15, 1945), by comparing these isomerides with the chlorocinnamic acids, one of which he obtained from chloroacetic acid by Perkin's synthesis, arrived at the conclusion that the acid of higher melting point is the true  $\alpha$ -bromocinnamic acid, whilst its isomeride is the  $\beta$ -bromocinnamic acid,  $\text{CBrPh}:\text{CH}\cdot\text{CO}_2\text{H}$ .

Stockmeir (*Beilstein*, 3rd ed., 2, 1411) recommends practically the same method as that employed by Glaser, whereas Kinnicutt (*Amer. Chem. J.*, 1882, 4, 26) states that very poor yields of the two acids are obtained by the action of alkali on cinnamic acid dibromide, and recommends the employment of the corresponding ethyl ester, when a 90 per cent. yield of the mixed bromocinnamic acids is obtained. Kinnicutt separated the two acids by fractional crystallisation from water, in which the  $\beta$ -acid (m. p.  $120^\circ$ ) is more readily soluble.

Michael and Brown, after preparing the two  $\beta$ -bromocinnamic acids by the addition of hydrogen bromide to phenylpropionic acid (*Ber.*, 1886, 19, 1378), concluded that both the acids obtained from cinnamic acid dibromide are  $\alpha$ -bromo-acids.

Erlenmeyer (*Ber.*, 1886, 19, 1936) has suggested that possibly certain of the acids are bimolecular, but this conclusion has been rendered untenable by the molecular weight determinations of the esters of these acids by Michael and Browne (*Ber.*, 1887, 20, 550).

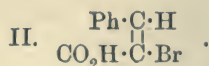
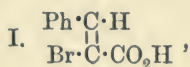
Anschütz and Selden (*ibid.*, 1388) have suggested that the acid melting at  $131^\circ$  is the true  $\alpha$ -acid, and that the so-called  $\beta$ -acid melting at  $120^\circ$  is structurally isomeric, having the formula  $\text{CHPh}:\text{CBr}:\text{C}\cdot\text{OH}$ .



The discovery of *allo*- and *iso*-cinnamic acids by Liebermann, and the introduction of the idea of stereochemistry among ethylene derivatives, led to the adoption of stereochemical formulæ for the two  $\alpha$ -bromo-acids.



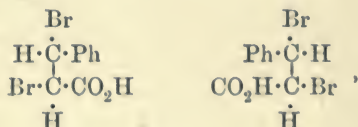
E. Erlenmeyer (*Ber.*, 1890, 23, 2130) showed that both acids, when oxidised with permanganate, yielded benzaldehyde, and should therefore both contain the bromine atom in the  $\alpha$ -position. He also proved that the more fusible acid is  $\alpha$ -bromo*isocinnamic* acid, since on reduction it yields Liebermann's *isocinnamic* acid, together with a certain amount of cinnamic acid. Liebermann (*Ber.*, 1895, 28, 134) obtained cinnamic acid by the reduction of the  $\alpha$ -acid melting at  $131^{\circ}$ , and hence concluded that it was  $\alpha$ -bromocinnamic acid. The formulæ for the two acids are thus:



Formula I is generally assigned to  $\alpha$ -bromocinnamic acid melting at  $131^{\circ}$ , whereas  $\alpha$ -bromo*allo*-(or *iso*-)\*cinnamic acid is represented by II. Most of the characteristic reactions and physical data are in harmony with these formulæ, for example, the *allo*-acid reacts readily with sulphuric acid to form a hydrindone derivative (Roser and Haseloff, *Ber.*, 1887, 20, 1577), whereas sulphuric acid does not readily decompose the  $\alpha$ -bromo-acid. The rates of esterification of the two acids (Sudborough and Lloyd, *Trans.*, 1898, 73, 91) are also in agreement with the views suggested by these configurations.

A strong argument brought against these formulæ by Michael is the fact that the  $\alpha$ -bromo-acid is transformed into phenylpropionic acid much more readily than the  $\alpha$ -*allo*-acid.

If the above configurations are correct, then cinnamic acid must be represented as  $\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{H} \\ || \\ \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$  and its dibromide must be the racemic compound.



and by elimination of hydrogen bromide,  $\alpha$ -bromo*allocinnamic* acid (m. p.  $120^{\circ}$ ) alone should result. All authorities are agreed that a mixture of the two  $\alpha$ -bromo-acids is obtained by the action of potassium hydroxide solution on the dibromide.

We have undertaken the study of different alkalis on the dibromide under varying conditions in order to determine ( $\alpha$ ) whether it is possible to obtain, under any given conditions, only the  $\alpha$ -bromo-

\* Michael's recent work would indicate that the halogenated *allo*-acids are, in reality, derivatives of *isocinnamic* acid; in view of Liebermann's criticisms (*Ber.*, 1903, 36, 176), the old notation is retained.

*allo*-acid, and (b) the conditions favourable to the formation of the  $\alpha$ -bromo-acid.

Some three years ago, it was noticed by one of us that the yield of  $\alpha$ -bromo-acid is largely increased when ethyl cinnamate dibromide is employed, and we have therefore continued the study of the action of alkalis on the different esters of the dibromide. During the progress of the work, a short note by Michael has appeared (*Ber.*, 1901, 34, 3666) in which attention is drawn to the influence of the ethyl group in the elimination of hydrogen bromide from cinnamic acid dibromide and its ester.

The experimental work which has been carried out with these objects in view may be classified under the following heads:

I. Preparation of cinnamic acid dibromide ( $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid) and its esters.

II. Separation of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-cinnamic acids.

III. Action of alkalis on cinnamic acid dibromide and its esters under varying conditions.

IV. Investigation of the bromocinnamene.

V. Transformations of  $\alpha$ -bromo*allo*cinnamic acid into  $\alpha$ -bromo-cinnamic acid.

### *I. Preparation of $\alpha$ : $\beta$ -Dibromo- $\beta$ -phenylpropionic Acid and its Esters.*

The method usually recommended for the preparation of this acid is the addition of the requisite amount of bromine to a carbon disulphide solution of cinnamic acid, and we find that for the preparation of small amounts of the dibromide this gives a very good yield; but although the dibromide is obtained pure when the crystals which separate from the solution are removed and washed with a little cold carbon disulphide, the process is somewhat inconvenient for the preparation of large quantities of the dibromide, as cinnamic acid is not readily soluble in the moderately cold solvent, and we have, therefore, adopted the following method for the preparation on a large scale.

From one to two hundred grams of finely powdered cinnamic acid are placed on a large clock glass in a desiccator over sulphuric acid, and a very slight excess of bromine, previously dried with sulphuric acid, is introduced in a small dish and the whole left for three days. When the weight of the acid has increased to the required extent, the product is crystallised from warm alcohol, as it always has a red colour. We have never observed the evolution of hydrogen bromide during the reaction and have obtained, after one crystallisation from alcohol,

almost theoretical yields of the pure acid melting and decomposing at 197°.\*

Michael states that small amounts of *allocinnamic acid dibromide* are obtained by the action of bromine on cinnamic acid, but using the method just indicated we have never been able to isolate any of this compound. In some cases, we obtained a small amount of oil by washing the crude dibromide with warm carbon disulphide. The solution, when cold, deposited a small amount of the ordinary dibromide, and when ultimately evaporated gave an oily residue amounting to less than 1 gram from 100 grams of cinnamic acid, from which no definite crystals could be obtained. The conditions of bromination were such that the production of any large amount of the *allo*-compound could not be expected.

*Methyl Cinnamate Dibromide (Methyl Dibromo- $\beta$ -phenylpropionate)*.—Methyl cinnamate, which was prepared by Fischer and Speyer's method (*Ber.*, 1895, 28, 3252), using a 4 per cent. solution of hydrogen chloride in methyl alcohol, was subsequently brominated in carbon bisulphide solution, and the dibromide, when purified by crystallisation from methyl alcohol, melted at 117°.

As the results obtained by the action of alcoholic potash on this ester were very different from those produced by the action of the same alkali on the acid dibromide, it was thought probable that the ester might not be a pure substance, but a mixture of two isomerides, and would therefore not correspond with the acid dibromide decomposing at 197°. This assumption did not appear at all probable, since the isomeric methyl dibromo- $\beta$ -phenylpropionate is already known and melts at 52–53° (Liebermann, *Ber.*, 1891, 24, 1107).

In order to be sure that the ester employed was the one corresponding with the acid decomposing at 197°, we have esterified cinnamic acid dibromide by the Fischer-Speyer method, 20 grams of cinnamic acid dibromide being boiled for 9 hours with 100 grams of methyl alcohol containing 4.5 grams of hydrogen chloride. On cooling, colourless, prismatic crystals separated, the weight of which was 11 grams. The melting point (116–117°) indicated that the substance was identical with the ester obtained by the addition of bromine to methyl cinnamate. A small amount of hydrogen chloride was passed into the liquid, from which the crystals had been

\* The melting points given in this communication were all determined by short normal thermometers, the whole of the thread of which was immersed in the bath. The temperature at which this acid melts and decomposes varies considerably with the method of heating. When slowly heated, it melts at 197°, but when quickly heated the thermometer may register a temperature as high as 207° before decomposition occurs.



removed, and it was boiled for a further period of 8 hours, when an additional 5.3 grams of the same ester were obtained.

In a second experiment, 30 grams of cinnamic acid dibromide and 60 c.c. of methyl alcohol under the foregoing conditions yielded 27 grams of the ester. The product thus obtained reacted with alcoholic potash in exactly the same manner as the ester produced by the addition of bromine to methyl cinnamate.

*Ethyl Cinnamate Dibromide (Ethyl Dibromo- $\beta$ -phenylpropionate).*—This ester has also been prepared by two distinct methods:

(a) Addition of bromine to a carbon disulphide solution of ethyl cinnamate.

(b) Alkylation of cinnamic acid dibromide by the aid of dry silver oxide and ethyl iodide.

The yield obtained by this second method was only 60 per cent. of the theoretical when the reaction was carried out in the cold, as secondary reactions occurred leading to the formation of an oil. This oil, when subjected to fractional distillation under reduced pressure, has been found to consist of ethyl cinnamate dibromide (m. p. 75–76°) and  $\omega$ -bromocinnamene.

As prepared by both methods, the ester crystallised from carbon disulphide in large, colourless prisms melting at 75–76°. Treatment with alcoholic potash gave results similar to those obtained with the methyl ester.

In a recent communication (*Ber.*, 1901, 34, 3660), Michael states that when ethyl cinnamate is brominated under suitable conditions the product may contain as much as 54 per cent. of ethyl *allo*-cinnamate dibromide melting at 28–30°.

As in most of our earlier experiments the yield of the dibromide melting at 75–76° was good, we determined to repeat the brominations, working as far as possible under the specified conditions, namely, low temperature, slight excess of bromine, absence of light, and in carbon tetrachloride solution. Even under these conditions, we have not been able to confirm Michael's results. The product obtained in each case, after removing the solvent in a desiccator over caustic soda at the ordinary temperature and under reduced pressure, consisted of a mass of large, prismatic crystals. In no case was the amount of oil appreciable, and the crude residue, which invariably melted at 66–74°, could therefore contain only the merest trace of the *allo*-dibromide, and when recrystallised from alcohol yielded the pure ester melting at 75–76°.

*Expt. 1.*—Eight grams of ethyl cinnamate were added to a solution of slightly more than the theoretical amount of bromine in well-cooled dry carbon disulphide. The mixture was allowed to

remain surrounded by ice for 24 hours and the solvent then removed under reduced pressure, the whole experiment being performed in the dark. The melting point of the slightly discoloured crude product was 69—72°; its weight was 15.1 grams.

*Expt. 2.*—Under similar conditions to Expt. 1, but with a larger excess of bromine, only a trace of oil was formed, whilst 13.3 grams of pure product melting at 75—76° were obtained after crystallisation from carbon disulphide.

*Expt. 3.*—In this case, carbon tetrachloride was used as solvent and only a slight excess of bromine was employed. The crystalline product, which was only slightly discoloured, weighed 15.4 grams and melted at 67—73°.

*Expt. 4.*—Similar to Expt. 3. The crude product, which weighed 14.9 grams, melted at 65—74°, and after recrystallising from carbon disulphide yielded 12.2 grams melting at 75—76°. The mother liquor, after evaporation, deposited large crystals of the ester melting at 75—76°, mixed with only a trace of oil.

*Expt. 5.*—A repetition of Expt. 1 gave 15.15 grams of ester melting at 67—75°. After recrystallisation, 12.6 grams of pure ester were obtained, and the solvent, on evaporation, left crystals of the ester mixed with very small amount of oil.

*Expt. 6.*—Ethyl cinnamate (8 grams) was placed in a stoppered bottle and 20 c.c. of carbon disulphide added, 7.7 grams of dry bromine were enclosed in a sealed bulb and placed in the bottle. The bottle was packed in a tin containing sawdust to prevent light affecting the reaction. The mixture was allowed to stand surrounded by ice for 2 hours, the bulb then broken by shaking, the bottle kept for 16 hours surrounded by ice, and the solvent finally removed as before. The weight of crude product melting at 67—73° was 14.5 grams, and on recrystallising from alcohol, 12.2 grams of ester melting at 75—76° were obtained. The mother liquor, on addition of water, gave an oily product which slowly solidified; this substance weighed 0.4 gram and melted at 35—60°.

*Expt. 7.*—Similar to Expt. 6, but the bottle was kept at 0° for 36 hours. Weight of product melting at 68—74° was 14.2 grams, and 12 grams of the pure recrystallised ester were obtained. The addition of water to the mother liquor precipitated an oil which subsequently solidified; the solution of this product in cold light petroleum (b. p. 30—60°) yielded on evaporation 0.2 gram of oil, which became solid and melted at 27—40°.

*Expt. 8.*—Similar to Expt. 7, but with carbon tetrachloride as solvent, the ester being sealed in the bulb. The crude product, which melted at 66—74° and weighed 13.6 grams, when recrystallised from alcohol gave 12 grams of ester melting at 75—76°. The oil

obtained from the mother liquor, when extracted with ligroin and carbon disulphide, gave 0.2 gram of a substance which solidified and melted at 30—40°.

We are not able to explain the difference between these results and those of Michael, as we followed as far as possible the conditions indicated by him and used carbon tetrachloride or carbon disulphide which had been thoroughly dried and freshly distilled.

In some of our experiments, the ester was added to the bromine solution, whereas in Michael's experiments the bromine was always added to the solution of the ester.

## II. *Separation of $\alpha$ -Bromo- and $\alpha$ -Bromoallo-cinnamic Acids.*

The methods employed by Kinnicutt and Glaser and described in the earlier part of this paper are tedious and of little value for the quantitative separation of the two acids. Preliminary experiments were therefore made in order to find some simple and rapid quantitative method of separation. The process which first suggested itself was the separation by the aid of the barium salts, as, according to Glaser, barium  $\alpha$ -bromocinnamate is very sparingly soluble and barium  $\alpha$ -bromoallocinnamate readily soluble in water.

Two grams of each were mixed, dissolved in ammonium hydroxide solution, and excess of fairly concentrated barium chloride solution was then added. The precipitated barium salt was collected, washed with barium chloride solution, and then decomposed with dilute hydrochloric acid; the liberated acid, when dry, was found to melt at 131° and the weight obtained was 1.97 grams. The filtrate containing the soluble barium salt was also acidified, and when dry the acid thus precipitated melted at 120° and weighed 1.85 grams. These results prove that the two acids may be completely separated by this method, but that a slight loss of both acids occurs. The amount of this is under two per cent. in the case of the  $\alpha$ -acid, whilst in that of the  $\alpha$ -allo-acid the loss is under eight per cent.

The mixtures of the two acids obtained by treating cinnamic acid dibromide with alkalis were invariably separated by the above method.

## III. *Action of Alkalis on $\alpha\beta$ -Dibromo- $\beta$ -phenylpropionic Acid and its Esters.*

The object to which our attention has been mainly directed in the course of this part of the work has been the determination of the manner in which the reaction between cinnamic acid dibromide and alkali is affected by (a) light, (b) increase in temperature, (c) vibrations



due to prolonged shaking, (d) the employment of the methyl, ethyl, *isobutyl*, and phenyl esters in place of the acid dibromide, (e) employment of different alkalis.

The general method adopted was as follows: the acid dibromide (10 grams) or an equivalent amount of an ester (10.45 grams of the methyl, 10.91 grams of the ethyl, or 11.83 grams of the *isobutyl* ester) was mixed with the calculated quantity of the alkali in aqueous or alcoholic solution; in all cases, two molecules of alkali were employed for each molecule of acid dibromide or ester. The mixture was kept under the special conditions enumerated in each experiment, the alcohol was removed by evaporation on the water-bath unless otherwise stated, and the dry mixture of alkali salts obtained was stirred with a little water. In no case did the whole of the residue dissolve, as nearly all the salts of  $\alpha$ -bromocinnamic acid are only sparingly soluble in water. An excess of barium chloride solution was added and the two acids separated by the method described above.

*(a and b) Influence of Light and Temperature.*

The following series of experiments prove that neither the nature of the reaction nor the relative amounts of the two acids produced are affected to any appreciable extent by the presence or absence of sunlight or by an increase in temperature amounting to 100°.

*Expt. 1.*—Ten grams of cinnamic acid dibromide were mixed at  $-10^{\circ}$  with the calculated amount of alcoholic potash (10 per cent. solution) and kept at  $-10^{\circ}$  to  $-5^{\circ}$  for 2 days, the whole experiment being conducted in the dark. At the end of that time, the cinnamic acid dibromide had wholly disappeared, but a precipitate had been formed. The alcohol was allowed to evaporate at the ordinary temperature and the residue separated in the usual manner. The weights of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-acids, melting at 128—130° and 110—117° respectively, were 0.75 and 5.85 grams.

The acids obtained directly from the barium salts were usually not quite pure, the  $\alpha$ -acid in all cases melted at 126—130° instead of 130—131°, and the  $\alpha$ -*allo*-acid usually at 115° instead of 120°. Each acid was obtained in a pure state after one crystallisation from a mixture of benzene and light petroleum or chloroform and light petroleum.

*Expt. 2.*—The conditions were the same as in *Expt. 1*, with the exception that the mixture, cooled to  $-5^{\circ}$ , was placed in fairly bright sunlight and occasionally shaken, the reaction being complete after about 28 hours. The weights of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-acids were 0.76 and 5.8 grams respectively.

*Expt. 3.*—Ten grams of the acid were mixed with the calculated amount of alcoholic potash, care being taken to avoid rise of tempera-

ture; the mixture was subsequently kept at the ordinary temperature for 3 hours, the whole of the experiment being carried out in the dark. The alcohol was evaporated on the water-bath; 0.83 gram of  $\alpha$ -bromo-acid and 5.8 grams of  $\alpha$ -bromoallo-acid were obtained.

*Expt. 4.*—The conditions were the same as in *Expt. 3*, with the exception that the experiment was carried out in the light, the mixture being shaken for 3 hours; 0.76 gram of  $\alpha$ -bromo-acid and 6.05 grams of  $\alpha$ -bromoallo-acid were obtained.

*Expt. 5.*—Ten grams of the acid dibromide were mixed with the calculated amount of alcoholic potash and boiled for 20 minutes in ordinary daylight; 0.8 gram of  $\alpha$ -bromo-acid and 5.2 grams of  $\alpha$ -bromoallo-acid were obtained.

*Expt. 6.*—The methyl ester (10.45 grams) was boiled for 6 minutes with the calculated amount of alcoholic potash; 3.85 grams of  $\alpha$ -bromo-acid and 2.7 grams of  $\alpha$ -bromoallo-acid were obtained.

*Expt. 7.*—As in *Expt. 6*, except that the mixture was shaken at the ordinary temperature for 3 hours; 4.15 grams of  $\alpha$ -bromo-acid and 2.64 grams of  $\alpha$ -bromoallo-acid were obtained.

It has already been stated that methyl cinnamate dibromide was also prepared by the direct esterification of the acid dibromide by the Fischer-Speyer method. The results obtained when this preparation was employed were similar to those of *Expts. 6* and *7*, in which the ester formed by the union of bromine and methyl cinnamate was used.

*Expt. 8.*—10.45 grams of the ester dibromide, obtained by esterification of the acid dibromide, were treated as in *Expt. 6*. The yield was 4 grams of the  $\alpha$ -bromo-acid and 2.7 grams of its isomeride.

### (c) *Influence of Rapid Vibration.*

It was thought possible that the vibrations and shock produced by shaking the medium in which the reaction was taking place might influence the yields of the two acids.

*Expts. 9–11*, which were carried out by the aid of a Dunstan-Dymond shaker, when compared with the previous experiments, appear to negative this assumption. The relative amounts of the two acids are not altered, either by violent agitation during the reaction or by prolonged shaking after the reaction is complete.

*Expt. 9.*—10.45 grams of the methyl ester were added to the calculated amount of alcoholic potash at the ordinary temperature and the mixture shaken for 6 hours; 4.25 grams of the  $\alpha$ -bromo-acid and 2.8 grams of the  $\alpha$ -bromoallo-acid were obtained.

*Expt. 10.*—Similar to *Expt. 9*, except that the shaking was continued for 20 hours. The yields were 4.20 and 2.78 grams of the  $\alpha$ -bromo-acid and its isomeride respectively.

*Expt. 11.*—Similar to *Expt. 9*, except that the alcoholic potash was added in two stages; 10.45 grams of the ester were mixed with one equivalent of alcoholic potash and shaken for 1 hour; a second equivalent of alkali was then introduced, and the shaking continued for another hour.

The yields were the same as in *Expt. 9*.

(d) *Replacement of Cinnamic Acid Dibromide by its Esters.*

The experiments already described indicate that the relative amounts of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-acids produced are greatly altered by employing an ester in place of the free acid dibromide.

Comparative experiments have been carried out by using cinnamic acid dibromide and its methyl, ethyl, *isobutyl*, and phenyl esters.

In each case, 10 grams of the acid dibromide or an equivalent quantity of ester were boiled for 5—6 minutes with the calculated amount of alcoholic potash. The results were as follows:

| Expt.                              | $\alpha$ -Bromo-<br>acid. | $\alpha$ -Bromo-<br><i>allo</i> -acid. | Expt.                                     | $\alpha$ -Bromo-<br>acid. | $\alpha$ -Bromo-<br><i>allo</i> -acid. |
|------------------------------------|---------------------------|--|---|---------------------------|--|
| 12 Cinnamic acid<br>dibromide...   | 0.84                      | 5.5                                    | 17 Ethylester di-<br>bromide.....         | 3.7                       | 2.65                                   |
| 13 Cinnamic acid<br>dibromide...   | 0.81                      | 5.4                                    | 18 <i>isoButyl</i> ester<br>dibromide ... | 3.6                       | 2.75                                   |
| 14 Methyl ester<br>dibromide...    | 3.8                       | 2.6                                    | 19 <i>isoButyl</i> ester<br>dibromide ... | 3.7                       | 2.9                                    |
| 15 Methyl ester<br>dibromide...    | 3.85                      | 2.7                                    | 23 Phenyl ester<br>dibromide ...          | 3.8                       | 2.04                                   |
| 16 Ethyl ester di-<br>bromide..... | 3.8                       | 2.64                                   |   |                           |  |

*Preparation of isoButyl Cinnamate and its Dibromide.*

As these compounds have not been previously described, we give a brief account of their preparation.

A slight excess of *isobutyl* alcohol was added to freshly prepared cinnamyl chloride; the reaction, when started by warming, progressed rapidly until all the chloride had disappeared. After warming on the water-bath for a few minutes, the ester was distilled under reduced pressure. As thus obtained, *isobutyl cinnamate* is an almost colourless liquid with an ethereal odour; it boils at 164—165° under 16—17 mm. pressure.

The dibromide was prepared by adding a very slight excess of bromine in carbon disulphide to a solution of the ester in the same



solvent; after 2 hours, the solution was left to evaporate spontaneously, and the residue purified by crystallisation from light petroleum.

*isoButyl cinnamate dibromide* crystallises from light petroleum (b. p. 30—60°) in aggregates of silky needles melting at 59—60°; it is also readily soluble in chloroform, carbon disulphide, and warm ligroin. 0.2532 gave 0.2646 AgBr; Br = 44.5.  $C_{13}H_{16}O_2Br_2$  requires 44.0 per cent.

The results obtained with phenyl cinnamate dibromide, melting at 127°, are somewhat different, and some of the experiments are therefore given in detail.

*Expt. 20.*—12.45 grams of the ester dibromide (equivalent to 10 grams of cinnamic acid dibromide), when boiled for 5 minutes with alcoholic potash (2 mols.), gave 3.1 grams of  $\alpha$ -bromo-acid melting at 128—130°, and 1.75 grams of  $\alpha$ -bromo*allo*-acid melting at 115—118°.

*Expt. 21.*—12.45 grams, when treated similarly, gave 3.3 grams of  $\alpha$ -bromo-acid and 1.55 grams of the *allo*-isomeride.

As the yields of the two acids were much less than the theoretical, and a considerable amount of an oily by-product was also observed, further experiments were carried out.

*Expt. 22.*—12.45 grams of the ester dibromide were boiled for 5 minutes with alcoholic potash (2 mols.), and after removing the alcohol the residue was dissolved with water and extracted with ether. From the aqueous solution, 3.35 grams of  $\alpha$ -bromo-acid and 1.65 grams of  $\alpha$ -bromo*allo*-acid were obtained. The ethereal extract, after being washed three times with dilute caustic soda solution to remove phenol, was dried and the solvent distilled off. The oily residue weighed 2.3 grams and boiled with decomposition at about 270°; with concentrated aqueous caustic potash, it gave, after some time, a clear solution, from which a mixture of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-acids was obtained by acidifying.

*Expt. 23.*—15.6 grams of the ester dibromide were added to cooled alcoholic potash (2 mols.) and the mixture shaken for 2 days at the ordinary temperature, when the alcohol was allowed to evaporate and the residue then treated as in *Expt. 22*.

3.85 grams of  $\alpha$ -bromo-acid and 0.90 gram of  $\alpha$ -bromo*allo*-acid were obtained, together with 4.35 grams of an oil which distilled over at 153—155° under 11—12 mm. pressure. The oil was left in contact with strong aqueous caustic potash for a day, when the hydrolysis was complete; the alkaline solution of potassium salts was treated in the usual manner with barium chloride, 0.90 gram of  $\alpha$ -bromo-acid and 1.65 grams of  $\alpha$ -bromo*allo*-acid being obtained.

The oil distilling at 153—155° under 11—12 mm. pressure must have been a mixture of the phenyl esters of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-cinnamic acids. This proves conclusively that in the case of the phenyl

dibromide the elimination of hydrogen bromide precedes the hydrolysis.

The fact that the oil consists mainly of the ester of the *allo*-acid would indicate that this ester is not so readily hydrolysed by alkalis as the ester of the isomeric  $\alpha$ -bromo-acid. This is interesting, as it has already been shown (Sudborough and Lloyd, *Trans.*, 1898, 73, 91) that the  $\alpha$ -bromo*allo*-acid is not so readily esterified as the isomeric  $\alpha$ -bromo-compound.

From the results given in the preceding table, it is obvious that the substitution of an ester for the free acid dibromide tends, in all cases, to increase greatly the amount of  $\alpha$ -bromocinnamic acid formed. When alcoholic potash is employed, the amount of  $\alpha$ -bromo-acid obtained from 10 grams of cinnamic acid dibromide is always less than 1 gram, but when an ester is used with the same alkali, the amount is more than quadrupled, and reaches nearly 4 grams.

As stated in the introduction, the normal compound, which should be formed by the elimination of hydrogen bromide from cinnamic acid dibromide, is  $\alpha$ -bromo*allo*-(or *iso*)-cinnamic acid, that is, the acid which on reduction yields *allo*-(or *iso*)-cinnamic acid. This has been shown by Erlenmeyer (*Annalen*, 1895, 287, 21) to be the acid melting at 120°, which is usually called  $\alpha$ -bromocallocinnamic acid. The results obtained when the acid dibromide is employed may be regarded as being in harmony with this theoretical deduction; the main product is  $\alpha$ -bromocallocinnamic acid, and only a small amount of the  $\alpha$ -bromocinnamic acid is obtained. The formation of this may be attributed to the fact that the *allo*-acid is unstable (see later experiments, p. 685), and either at the moment of its formation or afterwards becomes partially converted into the more stable  $\alpha$ -bromo-acid.

When the esters are employed, the chief product is the  $\alpha$ -bromo-acid, together with smaller amounts of the  $\alpha$ -bromo*allo*-acid. This undoubtedly points to the fact that the alkali does not first completely hydrolyse the ester and then eliminate hydrogen bromide, it being far more probable that the withdrawal of hydrogen bromide occurs before the hydrolysis. In the case of the phenyl ester, the withdrawal of hydrogen bromide before complete hydrolysis is proved by the foregoing experiments.

The fact that the chief product is  $\alpha$ -bromo-acid can be accounted for by assuming that the esters of the *allo*-acid are even less stable than the free acid, and therefore are more readily transformed into the esters of the  $\alpha$ -bromo-acid.

Michael (*loc. cit.*) has recently come to the conclusion that the ethyl cinnamate dibromide melting at 75–76° is the true dibromide of ethyl *allocinnamate*, and not that of ethyl cinnamate. This view is supported, to a certain extent, by his experiments on the addition of

bromine to ethyl cinnamate, but for some unknown reason our own experiments have not yielded similar results.

If we assume that the esters employed are not the dibromides of the esters of cinnamic acid, but of *allocinnamic* acid, then the chief product formed by the action of alkali should be the  $\alpha$ -bromo-acid. The production of the relatively large amount of the  $\alpha$ -bromo*allo*-acid presents a difficulty, as this is the less stable isomeride, and is not likely to be produced by the molecular rearrangement of the  $\alpha$ -bromo-acid. The fact that the esters we have employed undoubtedly correspond with the ordinary cinnamic acid dibromide decomposing at  $197^{\circ}$ , since this substance, when esterified, yields these compounds, is a further argument against the conclusion that these esters are derivatives of *allocinnamic* acid. Moreover, if the esters are derivatives of *allo*-cinnamic acid, then the acid dibromide itself is also an *allo*-compound, and it becomes a little difficult to reconcile this conclusion with the fact that the main product produced by the action of alkali is  $\alpha$ -bromo-*allocinnamic* acid.

(e) *Influence of Different Alkalis on the Reaction.*

Our earlier experiments were all carried out with alcoholic potash. In order to determine whether the nature of the alkali was an important factor in determining the yields of the two acids, we have made experiments with the following alkalis: caustic potash in alcoholic or aqueous solution, caustic soda in alcoholic solution, alcoholic sodium or potassium ethoxide, aqueous sodium carbonate, aqueous or alcoholic ammonia, aqueous baryta, and alcoholic dimethylaniline.

The esters reacted so slowly with aqueous solutions of the different alkalis, and also with alcoholic sodium ethoxide or dimethylaniline, that the products could not be investigated.

The experiments were carried out on the plan previously described, and the results obtained are given in the following table :

|                         | Alkali.             | Weight of<br>$\alpha$ -bromo-<br>acid. | Weight of<br>$\alpha$ -bromo-<br><i>allo</i> -acid. | Method.                     |
|-------------------------|---------------------|--|---|-----------------------------|
| Cinnamic acid dibromide |                     | 0.95                                   | 4.96  | } Boiling for 5 minutes     |
| " "                     |                     | 0.84                                   | 5.5   |                             |
| " "                     |                     | 0.81                                   | 5.4   |                             |
| " "                     | Alcoholic<br>potash | 0.80                                   | 5.69  | Boiling for 4 hours         |
| " "                     |                     | 0.76                                   | 6.10  | Shaking for 2 hours         |
| " "                     |                     | 0.76                                   | 6.05  |                             |
| " "                     |                     | 0.76                                   | 5.8   | At $-5^{\circ}$ in sunlight |
| " "                     |                     | 0.75                                   | 5.85  | At $-5^{\circ}$ in the dark |



|                         | Alkali.   | Weight of<br>$\alpha$ -bromo-<br>acid. | Weight of<br>$\alpha$ -bromo-<br>allo-acid. | Method.   |
|-------------------------|---|--|---|---|
| Cinnamic acid dibromide | Alcoholic<br>soda   | 1.61                                   | 4.85  | Boiling for 5 minutes   |
| “ “                     |   | 1.51                                   | 4.92  | “ “ “   |
| “ “                     |   | 1.62                                   | 4.93  | Shaking for 2 hours   |
| “ “                     | Sodium<br>ethoxide  | 0.91                                   | 5.89  | Shaking for 3 hours   |
| “ “                     |   | 0.84                                   | 6.01  | “ “   |
| “ “                     | Potassium<br>ethoxide   | 0.45                                   | 6.10  | Boiling for 5 minutes   |
| “ “                     |   | 0.50                                   | 5.87  | “ “   |
| “ “                     | Aqueous<br>potash   | 1.16                                   | 2.78  | { Shaking, no cooling<br>during addition.<br>Shaking, low tem-<br>perature. |
| “ “                     |   | 1.54                                   | 4.46  |   |
| “ “                     |   | 1.8                                    | 4.5   |   |
| “ “                     | Aqueous baryta..... Bromocinnamene, with a small<br>amount of the acids |  |   |   |
| “ “                     | Aqueous sodium car-<br>bonate..... Bromocinnamene only                  |  |   |   |
| “ “                     | Aqueous ammonia ... “ “   |  |   |   |
| “ “                     | Alcoholic ammonia ... Acid dibromide unaltered                          |  |   |   |
|                         | Alkali.   | Weight of<br>$\alpha$ -bromo-<br>acid. | Weight of<br>$\alpha$ -bromo-<br>allo-acid. | Method.   |
| Methyl ester dibromide  | Alcoholic<br>potash   | 3.8                                    | 2.6   | Boiling for 5 minutes   |
| “ “                     |   | 3.85                                   | 2.7   | “ “ “   |
| “ “                     |   | 4.25                                   | 2.8   | Shaking for 3 hours   |
| “ “                     |   | 4.15                                   | 2.64  | “ “   |
| “ “                     | Alcoholic<br>soda   | 3.93                                   | 2.3   | Boiling for 5 minutes   |
| “ “                     |   | 3.8                                    | 2.4   | “ “ “   |
| “ “                     |   | 4.25                                   | 2.6   | Shaking for 3 hours   |
| Ethyl ester dibromide   | Alcoholic<br>potash   | 3.78                                   | 2.64  | Boiling for 5 minutes   |
| “ “                     |   | 3.72                                   | 2.65  | “ “ “   |
| “ “                     |   | 3.8                                    | 2.68  | Boiling for 4 hours   |
| “ “                     |   | 3.7                                    | 2.8   | “ “ “   |
| “ “                     |   | 4.16                                   | 2.9   | Shaking for 3 hours   |
| “ “                     | Alcoholic<br>soda   | 3.53                                   | 2.55  | Boiling for 5 minutes   |
| “ “                     |   | 3.45                                   | 2.54  | “ “ “   |
| “ “                     |   | 4.10                                   | 2.89  | Shaking for 3 hours   |

The results obtained with dimethylaniline are somewhat curious, the products being cinnamic acid,  $\omega$ -bromocinnamene, and only a trace of a bromo-acid.

*Expt. 24.*—Ten grams of cinnamic acid dibromide were boiled for 45 minutes with a slight excess of an alcoholic solution of dimethylaniline (2 mols.). The alcohol was removed by evaporation and the residue acidified with hydrochloric acid. The precipitated acids were collected and washed, when an oil passed into the filtrate; this substance was bromocinnamene, which, after drying, weighed 1·6 grams; the acid on the filter-paper proved to be cinnamic acid, the yield being 3·07 grams.

*Expt. 25.*—Ten grams of the acid dibromide were boiled for 2 hours with an alcoholic solution of dimethylaniline and treated as in *Expt. 24*. 2·2 grams of cinnamic acid were obtained together with a large amount of oil.

*Expt. 26.*—19·48 grams of acid dibromide were treated as in *Expt. 25*, but the boiling was continued for  $1\frac{1}{2}$  hours. 2·8 grams of cinnamic acid were obtained together with 6·8 grams of bromocinnamene.

*Expt. 27.*—Ten grams of acid dibromide were added to alcoholic dimethylaniline, the mixture shaken for 6 hours, and the alcohol removed. The reaction was not complete, some unaltered acid dibromide still remained, but in this case also a large amount of oil was formed.

The oil obtained in each experiment proved to be  $\omega$ -bromocinnamene; it distilled at  $215\text{--}220^\circ$  under the ordinary pressure, and on bromination gave a dibromide melting at  $35\text{--}36^\circ$ .

#### *Cinnamic Acid Dibromide and Aqueous Ammonia.*

*Expt. 28.*—Ten grams of the dibromide were gradually added to the calculated amount of aqueous ammonia, the temperature being kept down by means of cold water. After a short time, the formation of oil was indicated by the odour. The mixture was left for a week in a corked flask, but the acid did not appear to have undergone appreciable alteration. The mixture was therefore warmed on the water-bath for a few minutes, an oil was immediately formed, this was extracted with ether, and after drying the extract, the ether was distilled off, when 3·7 grams of an oil were left; this product, which proved to be  $\omega$ -bromocinnamene, distilled almost entirely at  $215\text{--}217^\circ$ , and gave the dibromide melting at  $35\text{--}36^\circ$ . The filtrate, on acidifying, gave 0·02 gram of an acid which had no definite melting point.

*Expt. 29.*—Ten grams of the dibromide were gradually added to the calculated amount of aqueous ammonia, and the mixture left for three weeks. Some solid remained mixed with oil. On extraction

with ether, 2.0 grams of bromocinnamene were obtained with 2.7 grams of unaltered cinnamic acid dibromide decomposing at 194—196°.

*Cinnamic Acid Dibromide and Alcoholic Ammonia.*

*Expt. 30.*—Ten grams of acid dibromide were added to the calculated amount of alcoholic ammonia and the mixture left for a week. As the dibromide did not appear appreciably altered, the mixture was boiled for 5 minutes and the alcohol then evaporated on the water-bath. A white solid was left showing no trace of oil. The acid obtained from this by the addition of hydrochloric acid weighed 9.6 grams, and proved to be unaltered dibromide.

*Expt. 31.*—Ten grams of acid dibromide, when treated as in *Expt. 30*, with the difference that the mixture was left for three weeks instead of warming, gave 9.4 grams of unaltered dibromide decomposing at 194—196°.

*Cinnamic Acid Dibromide and Aqueous Sodium Carbonate.*

*Expt. 32.*—Ten grams of the acid dibromide were added slowly to the calculated amount of sodium carbonate solution, the mixture being left for a week, and then warmed for a few minutes, when an oil was produced; this product was extracted with ether, and from the ethereal solution, 3.6 grams of bromocinnamene were obtained.

From the filtrate, 0.02 gram of an acid was precipitated; this product melted indefinitely from 150° upwards.

*Expt. 33.*—Ten grams of acid dibromide were added to the calculated amount of sodium carbonate solution, and the mixture left for 3 weeks. The oil formed was then extracted with ether, and 3.8 grams of bromocinnamene were obtained; 0.4 gram of unaltered dibromide was recovered from the filtrate.

As the presence of excess of sodium carbonate might favour the formation of bromocinnamene, an experiment was carried out in which the acid dibromide was always in excess. The results obtained were similar to those of previous experiments.

*Expt. 34.*—The calculated amount of sodium carbonate solution was added drop by drop from a burette to 10 grams of the acid dibromide, and the mixture left for three weeks; 4.1 grams of bromocinnamene were obtained.

*Cinnamic Acid Dibromide and Aqueous Baryta.*

*Expt. 35.*—Five grams of acid dibromide were shaken for 5 hours with the calculated amount of aqueous baryta. Some bromocinnamene was formed, and unaltered acid dibromide remained.



*Expt. 36.*—Five grams of acid dibromide were shaken for 24 hours with the calculated amount of baryta; bromocinnamene was formed together with 0.23 gram of  $\alpha$ -bromocinnamic acid and 0.77 gram of an acid melting at 170—184° with decomposition, this substance being probably unaltered cinnamic acid dibromide.

#### IV. *Bromocinnamene.*

Barish was the first to note the formation of a bromocinnamene by the action of alcoholic potash on cinnamic acid dibromide. The quantity thus obtained is usually small, but by altering the conditions the amount may be largely increased. The production of only a minute quantity of the bromocinnamene can be readily detected by the characteristic odour. We have noticed its formation from the acid dibromide under the following conditions: action of (i) alcoholic or aqueous caustic potash; (ii) alcoholic potash at high temperatures; (iii) aqueous ammonia, baryta, or sodium carbonate, especially at higher temperatures; (iv) alcoholic dimethylaniline. The substance is also produced during the esterification of the dibromide by the aid of dry silver oxide and ethyl iodide, and also by the action of dimethylaniline on  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-cinnamic acids.

The factors which tend to increase the amount of bromocinnamene are (a) employment of the acid dibromide and not its esters; (b) relatively high temperature; (c) employment of aqueous, rather than alcoholic, solutions of alkalis; (d) employment of a feeble, rather than a strong alkali.

Contrary to Kinnicutt's statement, we have found that good yields of the two  $\alpha$ -bromocinnamic acids may be obtained by the action of alcoholic, and even of aqueous caustic potash on cinnamic acid dibromide, provided that the temperature is not allowed to rise.

The bromocinnamene obtained in all these experiments is identical with the compound obtained by boiling cinnamic acid dibromide with water, and is  $\beta$ - or  $\omega$ -bromocinnamene ( $\alpha$ -bromo- $\beta$ -phenylethylene) (Fittig and Binder, *Annalen*, 1879, 195, 141; Nef, *Annalen*, 1899, 308, 267). It is most readily characterised by transformation into its dibromide, which crystallises from light petroleum in needles melting at 37—38°. In Beilstein's *Handbuch* (2nd edition), this compound is termed  $\alpha$ : $\beta$ : $\beta$ -tribromoethylbenzene, but the proper correction has been made in the Supplement, and also in Richter's *Lexicon*. The oils obtained under the foregoing conditions gave practically quantitative yields of this solid dibromide, thus proving that none of them contained appreciable amounts of the isomeric  $\alpha$ -bromocinnamene.

Barish attributed the formation of the bromocinnamene to the elimination of carbon dioxide from one or both of the  $\alpha$ -bromo-acids.

A number of experiments made by us tend to render this view untenable. We have boiled cinnamic acid dibromide and its ethyl ester for 5 minutes, and for 4 hours with the calculated amount of alcoholic potash, and the yield of  $\alpha$ -bromo- and  $\alpha$ -bromoallo-acids has not been affected by the prolonged heating.

|  | Time.     | $\alpha$ -Bromo-acid. | $\alpha$ -Bromoallo-acid. |
|--|-----------|-----------------------|---------------------------|
| 10 grams cinnamic acid dibromide ..... | 5 minutes | 0.80 gram             | 5.69 grams                |
| 10 grams cinnamic acid dibromide ..... | 4 hours   | 0.84 „                | 5.5 „                     |
| 10.91 grams ethyl ester ...            | 5 minutes | 3.78 grams            | 2.64 „                    |
| 10.91 grams ethyl ester ...            | 4 hours   | 3.8 „                 | 2.68 „                    |

Similarly, when the pure  $\alpha$ -bromo- or  $\alpha$ -bromoallo-acid is boiled with alcoholic potash (1 mol.) for several hours, no trace of decomposition occurs, and even when an excess of alkali is employed the product produced from the  $\alpha$ -bromo-acid is phenylpropionic acid, whereas the allo-acid is practically unaffected.

It would thus appear that the bromocinnamene is not a secondary decomposition product obtained by the elimination of carbon dioxide from one of the  $\alpha$ -bromo-acids, but is a primary decomposition product. Experiments have proved that those alkalis, aqueous baryta, aqueous sodium carbonate, and aqueous caustic potash, for example, which readily yield  $\omega$ -bromocinnamene from the dibromide, are practically without action on the  $\alpha$ -bromo-acids; in all these cases, the solution of the acids were shaken for several days with the alkali, and practically the calculated amount of unaltered acid (either  $\alpha$ -bromo- or  $\alpha$ -bromoallo-) was recovered, and no odour of the bromocinnamene was noticed. When the  $\alpha$ -bromo-acids were boiled with alcoholic dimethylaniline (2 mols.), nearly the calculated amount of unaltered acid was obtained. A minute trace, however, of oil was formed in each case—less than 0.1 gram from 5 grams of acid—and this was proved to be  $\omega$ -bromocinnamene by conversion into its dibromide melting at 37–38°. This may be taken as a further proof of the position of the bromine atom in the bromocinnamene.

It is highly probable that the elimination of hydrogen bromide and the withdrawal of carbon dioxide, required for the production of bromocinnamene from cinnamic acid dibromide, occur simultaneously. The experiments described above indicate that the elimination of hydrogen bromide does not precede the loss of carbon dioxide.

If carbon dioxide were eliminated before the hydrogen bromide, cinnamene dibromide would be first formed, and this, by the loss of hydrogen bromide, might then yield  $\omega$ -bromocinnamene. That this

does not occur is proved by the fact that cinnamene dibromide, on treatment with alkali, yields  $\alpha$ -bromocinnamene,  $\text{CPhBr}\cdot\text{CH}_2$ , or, according to Nef (*Annalen*, 1899, 308, 273), a mixture of  $\alpha$ - and  $\omega$ -bromocinnamenes. In our experiments, we have not been able to find any trace of the  $\alpha$ -compound.

#### V. Transformation of $\alpha$ -Bromoallocinnamic Acid into $\alpha$ -Bromocinnamic Acid.

This transformation has been accomplished by three methods, namely, (a) action of sunlight on the dry acid; (b) action of sunlight on an aqueous solution of the barium salt; (c) action of heat on the free acid.

*Action of Light on the Acid.*—One gram of the  $\alpha$ -*allo*-acid, in the form of glistening, flat plates, was exposed between watch-glasses to ordinary diffused daylight on August 28th, 1900. It was noticed that the crystals gradually lost their lustre and became opaque on the surface. On November 1st, the melting point had sunk to  $96^\circ$ , and by December 10th, to about  $90^\circ$ . The mixture of acids was then transformed into barium salts, which were separated in the usual manner, 0.22 gram of  $\alpha$ -bromocinnamic acid melting at  $131^\circ$  being thus obtained.

*Action of Light on Barium  $\alpha$ -Bromoallocinnamate in Aqueous Solution.*—As the barium salt of  $\alpha$ -bromocinnamic acid is almost insoluble in water, it was thought possible that the barium salt of the *allo*-acid might be quantitatively transformed into the isomeric barium salt by exposure of its aqueous solution to sunlight. The following experiments indicate that this is, to a large extent, true.

One gram of  $\alpha$ -bromoallocinnamic acid was dissolved in a slight excess of dilute ammonia, and excess of barium chloride solution added, the total volume of liquid being about 10 c.c. The solution was exposed to fairly bright sunlight in a south-west window on September 9th, 1901. Well-defined crystals of barium  $\alpha$ -bromocinnamate began to separate after two days. The solution was examined on October 25th, and the acids separated in the usual manner. 0.29 gram of  $\alpha$ -bromocinnamic acid melting at  $131^\circ$  and 0.7 of unaltered *allo*-acid melting at  $119$ – $120^\circ$  were obtained.

Two grams of the  $\alpha$ -*allo*-acid were dissolved in slight excess of baryta solution, and the excess of baryta precipitated as carbonate by leaving the solution in an atmosphere of carbon dioxide. The clear solution was then placed in a corked flask and exposed to sunlight in a south window on June 4th, 1902. After two days, crystals appeared; the solution was left until September 29th, when the crystals were removed and yielded 1.98 grams of  $\alpha$ -bromocinnamic acid melting at  $130$ – $131^\circ$ .



The clear filtrate from the crystals, when acidified, gave no trace of unaltered *allo*-acid.

*Effect of heating  $\alpha$ -Bromoallocinnamic Acid.*—Michael states (*Ber.*, 1901, 34, 3648) that the  *$\alpha$ -allo*-acid is completely transformed into the isomeric  *$\alpha$ -bromo*-acid when a mixture of the two acids is kept in the liquid state for 1 minute. Some of our earlier experiments indicated that the transformation does not take place nearly so readily as suggested by Michael, and we have made a more careful study of this transformation.

The following table gives a list of the experiments made in order to determine (*a*) the temperature and (*b*) the time required for practically complete transformation. The method of procedure was as follows: 5 grams of pure  *$\alpha$ -bromoallocinnamic acid* were placed in a test-tube provided with a loosely-fitting cork which carried a thermometer. The test-tube was then plunged into a sulphuric acid bath heated to the required temperature, and the time measured from the moment when the thermometer placed in the molten acid indicated the fixed temperature. The mixture of acids was separated in the usual manner by the aid of their barium salts.

| Temperature. | Time in minutes. | Weight of <i><math>\alpha</math>-bromoallo-</i> acid. | Weight of <i><math>\alpha</math>-bromo</i> -acid. |
|--------------|------------------|---|---|
| 132—133°     | 10               | 4.76  | 0.05  |
| 132—133      | 30               | 4.61  | 0.23  |
| 143—144      | 12               | 4.70  | 0.12  |
| 143—144      | 30               | 4.50  | 0.35  |
| 155          | 10               | 4.59  | 0.22  |
| 155          | 30               | 4.08  | 0.72  |
| 165          | 10               | 4.38  | 0.46  |
| 175          | 10               | 3.96  | 0.85  |
| 185          | 10               | 3.65  | 1.18  |
| 196          | 10               | 1.86  | 2.85  |
| 203—204      | 10               | 0.73  | 4.11  |

It is obvious from these results that the transformation is not complete even when the *allo*-acid is heated at 203—204° for 10 minutes. Michael's statement that a complete transformation is effected by keeping the  *$\alpha$ -allo*-acid in a molten state for 1 minute must be incorrect. We have examined some of the numbers obtained in the transformation of the  *$\alpha$ -allo*-acid in order to see whether the change may be included amongst the ordinary unimolecular reactions. The numbers in the following table indicate that the reaction is unimolecular:

| Temp. | Time in minutes. | Weight of $\alpha$ -bromoallo-acid taken. | Weight of $\alpha$ -bromo-acid formed. | $1/t \log a/a - x$ . |
|-------|------------------|---|--|----------------------|
| 155°  | 10               | 5   | 0.26                                   | 0.00232              |
| 155   | 30               | 5   | 0.76                                   | 0.00238              |
| 155   | 45               | 5   | 1.05                                   | 0.00227              |
| 155   | 60               | 5   | 1.41                                   | 0.00239              |
| 155   | 60               | 5   | 1.39                                   | 0.00236              |

The amount of bromo-acid given in the table is the actual weight of acid obtained *plus* the portion retained in solution. The experiments proved that the amount remaining in solution was practically 0.04 gram for the amount of liquid employed in each experiment.

### Conclusion.

The more important results obtained in the course of this investigation may be summarised as follows:

1. Only minute amounts of an *allo*-compound are obtained by the addition of bromine to ethyl cinnamate.

2. Good yields of  $\alpha$ -bromo- and  $\alpha$ -bromoallocinnamic acids may be obtained by the action of alcoholic potash on cinnamic acid dibromide or its esters. When the acid dibromide is employed, it is advisable to work at the ordinary temperature and to keep the mixture cool.

3. The relative amounts of the two acids vary considerably when an ester is employed in place of the acid dibromide. The use of the ester increases the amount of  $\alpha$ -bromo-acid, and all the esters investigated, the methyl, ethyl, isobutyl, and phenyl esters, behave in exactly the same way.

4. The relative amounts of the two acids are also affected to a less extent by the nature of the alkali and of the solvent (either alcohol or water).

5. A by-product often obtained is  $\omega$ -bromocinnamene. This is produced (*a*) when the temperature is raised, (*b*) when aqueous solutions or feeble alkalis are employed.

6. The bromocinnamene is produced directly from the cinnamic acid dibromide and not from the  $\alpha$ -bromo-acids.

7. The  $\alpha$ -bromo- and  $\alpha$ -bromoallo-acids are most readily separated by means of their barium salts.

8. The  $\alpha$ -bromoallo-acid may be transformed into the isomeric acid by sunlight or by heat, but the transformation by the latter method does not occur as readily as is stated by Michael.

LXIX.—*The Diazo-reaction in the Diphenyl Series.*  
*Part I. On Dianisidine and 3 : 3'-Dichlorobenzidine.*

By JOHN CANNELL CAIN.

IN measuring the rate of decomposition of diazo-salts prepared from certain diamines of the diphenyl series, it was noticed (Cain and Nicoll, *Trans.*, 1902, 81, 1440) that the substances obtained by heating an aqueous solution of the diazonium salts derived from dianisidine and *o* : *o*-dichlorobenzidine were coloured and insoluble in alkali.

It was obvious that the reaction did not proceed as in the case of benzidine and tolidine which, like benzidine-3 : 3'-dicarboxylic acid, yield the corresponding dihydroxy-compounds (Bülow, *Ber.*, 1898, 31, 2577).

In the case of dianisidine, this anomalous behaviour has been described by Starke (*J. pr. Chem.*, 1899, [ii], 59, 204) in the following terms: "Die Bildung eines Diphenols . . . Konnte ich trotz vieler Versuche nicht erreichen, selbst beim Kochen der Tetrazo-dianisylchlorids mit bei 140° siedender Schwefelsäure liess sich die Bildung eines Phenols nicht beobachten." This chemist did not, apparently, examine the product of the reaction.

The decomposition of the diazo-salt from dichlorobenzidine by the usual methods results in the formation of a brownish-red, amorphous substance; in the case of dianisidine, the product is almost black, whilst both are quite insoluble in alkalis or the ordinary solvents and neither sublime nor melt on heating. These products, which are not attacked by the usual reducing agents, appear to form addition compounds with hydriodic acid.

Many experiments were made with the object of avoiding the formation of these substances in order to obtain the hydroxy-derivatives, but only in the case of dichlorobenzidine was it possible to isolate a minute quantity of such a substance by carrying out the experiment in very strong sulphuric acid solution. Although the investigation of these amorphous, insoluble compounds is, of necessity, very difficult, yet there does not seem to be much doubt that they are of a quinonoid character; the deep colour of both substances points to this conclusion, as does also their striking resemblance to certain compounds, the constitution of which must be of this nature.

Thus, Palmer and Grindley (*Ber.*, 1893, 26, 2304) obtained by the oxidation of penta-aminobenzene a deep brown, amorphous substance,



which was insoluble in all the ordinary solvents and did not melt; its empirical formula agreed with that of a triaminoquinone. Reduction experiments are not described.

Biginelli (*Gazzetta*, 1897, 27, 347) also has shown that on diazotising 5:8-diamino-6-methoxycoumarin, 7-amino-6-methoxycoumarin, the trimethyl ether of monaminopyrogallol, as well as Nietzki and Prousser's 2:5-diamino-1:4-diacetoxybenzene, deeply coloured (red or black) insoluble and infusible substances are obtained, which are regarded as condensation products from two molecules, thus:  $2R \cdot NH_2$  (on diazotisation)  $\rightarrow R \cdot NH \cdot O \cdot R$ . Biginelli supposes that the presence of methoxyl groups impedes diazotisation, and that during the diazotisation of such compounds, condensation products are mainly formed.

However, this conclusion certainly does not apply to the cases of dianisidine (3:3'-dimethoxybenzidine) and *o*-anisidine, which, as is well known, can be easily and quantitatively diazotised.

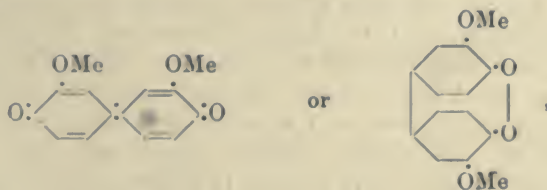
I have not been able to reduce the substances thus obtained from dichlorobenzidine and dianisidine, but by long continued boiling with strong hydriodic acid and red phosphorus an addition product resulted in each case, from which, however, hydriodic acid was eliminated by the action of water or alkalis.

Sulphuric and hydrochloric acids had no action on the original substances. Acetic anhydride gave an addition product, which was also easily decomposed by alkalis.

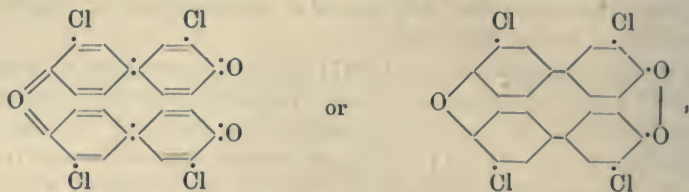
The reaction with hydriodic acid may perhaps confirm the quinonoid nature of the compounds, as many coloured substances having the properties of quinones, such as aurin, hæmatein, and brazilein, form addition compounds with certain acids, these being easily separated with water.

Nietzki (*Ber.*, 1895, 28, 56) suggests that such addition products may, in the case of ordinary quinone and hydrochloric acid, be represented thus:  $O:C_6H_4:O + HCl = \begin{smallmatrix} OH \\ | \\ Cl \end{smallmatrix} > C_6H_4:O$ , but the oxonium formula,  $\begin{smallmatrix} H \\ | \\ Cl \end{smallmatrix} > O:C_6H_4:O$ , may be equally applicable.

The substance derived from dianisidine may accordingly have the formula:



and that from dichlorobenzidine may be represented by :



the former structure being, in each case, the more probable.

### EXPERIMENTAL.

#### *Experiments with 3:3'-Dichlorobenzidine.*

3:3'-Dichlorobenzidine (12.6 grams) was dissolved in water with the addition of 30 c.c. of hydrochloric acid of sp. gr. 1.16, the solution being cooled, diazotised with 6.9 grams of sodium nitrite, and then filtered and decomposed either by direct heating or by adding it slowly to boiling dilute sulphuric acid.

In either case, a reddish-brown, amorphous substance was obtained in good yield, and no other product could be detected in the filtrate. The substance is quite insoluble in alkalis, acids, water, alcohol, ether, benzene, acetone, chloroform, ligroin, amyl alcohol, phenol, nitrobenzene, or pyridine. On heating, it does not melt, but gradually chars and burns away. After washing and drying, the following numbers were obtained :

0.1406 gave 0.3040  $\text{CO}_2$  and 0.0369  $\text{H}_2\text{O}$ .  $\text{C} = 58.98$  ;  $\text{H} = 2.94$ .

0.1824 „ 0.3909  $\text{CO}_2$  „ 0.0468  $\text{H}_2\text{O}$ .  $\text{C} = 58.45$  ;  $\text{H} = 2.88$ .

0.1419 „ 0.1675  $\text{AgCl}$ .  $\text{Cl} = 29.18$ .

0.1703 „ 0.2022  $\text{AgCl}$ .  $\text{Cl} = 29.36$ .

$\text{C}_{24}\text{H}_{12}\text{O}_8\text{Cl}_4$  requires  $\text{C} = 58.80$  ;  $\text{H} = 2.45$  ;  $\text{Cl} = 28.95$  per cent.

The substance would thus appear to be a quinone-anhydride having the formula indicated above. No reduction could be effected by any of the ordinary energetic reducing agents.

By boiling with hydriodic acid and red phosphorus, it was converted into a pale yellow, amorphous addition compound which was separated from the heavier red phosphorus by elutriation. This product was quite insoluble in all the ordinary solvents and did not melt, but hydriodic acid was eliminated on boiling with water or alkalis.

The analyses of the product containing iodine were not concordant, the amount of hydriodic acid absorbed evidently depending on the concentration. The largest amount found was 11.96 per cent., whereas  $(\text{C}_{24}\text{H}_{12}\text{O}_8\text{Cl}_4)_2 + \text{HI}$  requires 11.45 per cent. of iodine.

In an experiment with weaker acid, the iodine determination by the

Carius process gave 5.54 per cent., whilst, after boiling the substance with caustic soda solution, filtering, and estimating the sodium iodide by precipitation with silver nitrate, the iodine obtained was 5.66 per cent. Thus the substance in question is a true addition product, the residue after hydrolysis consisting apparently of the original substance.

By boiling with acetic anhydride and sodium acetate for some hours, an addition product was obtained which was of a much lighter colour than the original substance, but resembled it as regards its infusibility and its insolubility in the ordinary solvents:

0.1181 gave 0.1189 AgCl.  $\text{Cl} = 24.9$ .

$\text{C}_{24}\text{H}_{12}\text{O}_3\text{Cl}_4 + \text{C}_4\text{H}_6\text{O}_3$  requires  $\text{Cl} = 23.9$  per cent.

The original red substance was apparently regenerated on boiling with dilute caustic soda.

#### *Formation of 3:3'-Dichloro-4:4'-dihydroxydiphenyl.*

3:3'-Dichlorobenzidine is diazotised in a concentrated aqueous solution, using sulphuric acid instead of hydrochloric acid, and to the filtered solution, twice its volume of strong sulphuric acid is added. The mixture is now heated until the evolution of nitrogen ceases, when a tarry substance separates out. Under these conditions, no formation of the reddish-brown insoluble substance takes place. The tar is collected and extracted repeatedly with boiling water; the aqueous solution deposits white needles on cooling, the yield being very small.

The new substance is readily soluble in alkalis, being reprecipitated by acids; it is sparingly soluble in hot water and crystallises from this solvent in fine white needles melting at  $124^\circ$  (uncorr.). It dissolves very easily in ether, alcohol, benzene:

0.1250 gave 0.1420 AgCl.  $\text{Cl} = 28.09$ .

0.1322 „ 0.1503 AgCl.  $\text{Cl} = 28.11$ .

$\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2$  requires  $\text{Cl} = 27.81$  per cent.

This substance appears to be identical with one of the products obtained by Schmidt and Schultz (*Ber.*, 1879, 12, 490; *Annalen*, 1881, 207, 334) by the action of phosphorus pentachloride on  $\gamma$ -diphenol. A very small quantity of a white substance melting at  $126^\circ$  was thus produced; this compound, which was not analysed, being taken to be a trichlorodiphenol.



*Experiments with Dianisidine.*

A dilute solution of the diazonium salt was prepared as above by substituting 12.2 grams of dianisidine for the dichlorobenzidine. On boiling, a very dark brown, amorphous substance separated which was filtered and dried. This product resembles the corresponding derivative from dichlorobenzidine in being infusible, and also insoluble in alkalis and all the ordinary solvents:

0.1735 gave 0.4386  $\text{CO}_2$  and 0.0765  $\text{H}_2\text{O}$ .  $\text{C} = 68.96$ ;  $\text{H} = 4.90$ .

$\text{C}_{14}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 68.82$ ;  $\text{H} = 4.96$  per cent.

By boiling with hydriodic acid and red phosphorus, a light brown addition product is formed which easily loses hydriodic acid on warming with caustic soda solution. No reduction product could be obtained.

On warming with acetic anhydride and sodium acetate, a reddish-brown, insoluble addition product was obtained, from which the original substance was regenerated by boiling with dilute aqueous caustic soda.

Many experiments which were made in the hope of obtaining the dihydroxy-compound, especially by heating the concentrated diazo-solution with strong sulphuric acid, were unsuccessful.

The two diazo-groups of diazotised dichlorobenzidine decompose with water at the same rate, whilst those of diazotised dianisidine decompose at very different rates (Cain and Nicoll, *loc. cit.*).

It might, therefore, be expected that differently constituted condensation products would be formed from the two diazonium salts, and this anticipation has been confirmed by the results obtained in the foregoing experiments.

I hope to be able to extend these investigations to the mono-*ortho*-substituted diamines of the same series.

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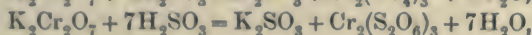
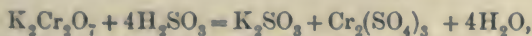
## LXX.—*The Mechanism of the Reduction of Potassium Dichromate by Sulphurous Acid.*

By HENRY BASSETT, jun., B.Sc., A.I.C.

BERTHIER, who investigated the action of sulphur dioxide on solutions of potassium dichromate and potassium chromate (*Ann. Chim. Phys.*, 1843, 7, 77), stated that in both instances a

mixture of sulphate and dithionate was formed. In the case of the chromate solution, a precipitate of brown chromium hydroxide, which was first formed, dissolved when more sulphur dioxide was passed into the liquid. As Berthier gave no details of his work and as the reduction of potassium dichromate and chromate by sulphurous acid has not, so far as I can discover, been studied since his time, it seemed desirable to investigate the reaction in greater detail.

The two reactions involving the formation of sulphate and dithionate should no doubt be represented in the following manner :



with similar equations for the reduction of potassium chromate and chromic acid.

### EXPERIMENTAL.

Solutions containing known amounts of sulphurous acid and of potassium dichromate were mixed and the excess of sulphurous acid estimated with iodine and sodium thiosulphate or the residual chromate with ferrous ammonium sulphate. In this way, the potassium sulphite will obviously be estimated along with the sulphurous acid, and from the amount of sulphurous acid oxidised by a known quantity of dichromate the relative amounts of sulphate and dithionate found can be calculated, the above equations indicating that the amount of sulphurous acid needed to produce dithionate is double that required to form sulphate.

The sulphurous acid solution, prepared by bubbling sulphur dioxide through air-free water, was kept in a bottle from which any desired quantity could be blown into a pipette by a current of carbon dioxide, and was standardised daily by adding 5 c.c. to excess of standard iodine solution and titrating with a standard sodium thiosulphate solution; the strength, which was found to remain very constant, diminished by only 0.7 per cent. in three weeks.

The experiments were performed so as to avoid all possible loss of sulphurous acid. An Erlenmeyer flask containing a known volume of standard chromate solution was furnished with a rubber cork, into which were fitted a T-piece connected with a Kipp's apparatus, a burette containing standard iodine solution, and a glass tube leading to a flask containing standard iodine solution with an outlet tube dipping into a small flask or beaker containing potassium iodide. The air in the apparatus was displaced by a rapid current of carbon dioxide from the Kipp's apparatus, and the top of the T-piece closed by a piece of glass rod and rubber tubing. A pipette with a slender stem was next filled with the sulphurous acid solution, the glass rod was

removed (whilst a very slow current of carbon dioxide was sent through the apparatus), and the stem of the pipette fitted into the T-piece. The acid solution being discharged into the flask, the pipette was rapidly withdrawn and the glass rod replaced. The flask was then shaken and 50 c.c. of standard iodine solution added, whilst any sulphur dioxide escaping from the liquid was carried over into standard iodine and thus recovered. After a few minutes, the apparatus was disconnected, the solutions mixed and titrated with standard thio-sulphate solution, a well-defined end point being obtained with starch as indicator in spite of the green colour of the chromium solutions.

Standard solutions of potassium dichromate and chromate were made by weighing out directly the recrystallised salts, whilst the chromic acid solutions, prepared from the pure trioxide (free from sulphuric acid), were standardised by titration against ferrous ammonium sulphate. The purity of these reagents was also checked by gravimetric estimations of the chromium as lead chromate.

### *Preliminary Experiments.*

On adding excess of sulphurous acid to solutions of potassium dichromate, potassium chromate and chromic acid, a clear green solution is obtained, and, judging by the change of colour, the reduction is instantaneous; this solution slowly becomes violet, but the change takes several weeks.

In these preliminary experiments, very weak solutions were reduced, and on testing with barium chloride in the cold no precipitate was obtained, whence it must be concluded that no  $\text{SO}_4$  ions were present. At first sight, this result seemed to suggest that no sulphate had been formed, but only dithionate. However, on estimating the quantity of sulphurous acid oxidised by a known amount of dichromate in the manner described, it was found that very little more sulphurous acid than was necessary to form chromium sulphate had been oxidised. Hence the amount of dithionate produced can only be small.

If dilute ammonia solution is gradually added to some of the reduced dichromate, no precipitate of chromium hydroxide appears at any point, and consequently no chromium ions are present. The solution, however, always gives a precipitate with platinic chloride, thus indicating the presence of potassium ions.

If, however, the reduced dichromate solution was heated to boiling for a few minutes or allowed to stand for several hours before testing with barium chloride or ammonia, a precipitate was always obtained immediately, showing that a profound change had taken place in the solution.

When moderately concentrated solutions are employed, a precipitate



is always obtained with barium chloride in the cold; thus, 10 c.c. of potassium dichromate (containing 0.245 gram of  $K_2Cr_2O_7$ ), when mixed with 10 c.c. of sulphurous acid solution (containing 0.2796 gram of  $H_2SO_3$ ), gave an immediate precipitate. If, however, some dilute hydrochloric acid was added before the barium chloride, no precipitate was obtained, showing that even in this case  $SO_4$  ions were absent.

When sulphurous acid is added to excess of chromic acid or potassium dichromate or chromate, the dark greenish-brown solution produced does not give the reactions of chromium or  $SO_4$  ions when treated in the foregoing manner. The dark solutions obtained from potassium dichromate and chromate still contain sulphite as they decolorise potassium permanganate and iodine solutions. If, however, they are acidified before or after adding the sulphurous acid, the resulting solution no longer contains sulphite. Solutions containing excess of chromic acid do not, under any conditions, decolorise permanganate or iodine.

### *Analytical Experiments.*

In all the following experiments, the various solutions were added in the order given, and in those indicated in the first two tables the solutions have the following concentration: in 10 c.c.,  $K_2Cr_2O_7 = 0.245$  gram and  $H_2SO_3 = 0.2852$  gram. The iodine solution was 0.0937-normal.

|  | Excess of<br>$H_2SO_3$ . | $H_2SO_3$<br>used up. | Mols. of<br>$H_2SO_3$ used<br>by 1 mol. of<br>$K_2Cr_2O_7$ . |
|--|--------------------------|-----------------------|--|
| 10 c.c. $K_2Cr_2O_7$ + 10 c.c. $H_2SO_3$ + 50 c.c.<br>iodine ..... | 0.0645 gram              | 0.2207 gram           | 3.24   |
| 10 c.c. $H_2SO_3$ + 10 c.c. $K_2Cr_2O_7$ + 50 c.c.<br>iodine ..... | 0.0636 "                 | 0.2216 "              | 3.25   |

If only sulphate were formed, 0.245 gram of potassium dichromate would oxidise 0.2044 gram of sulphurous acid, one mol. of  $K_2Cr_2O_7$  requiring 3 mols. of reducing agent. In these experiments, the iodine solution was added directly after mixing the dichromate and sulphurous acid solutions, and immediately titrated. It was found that the longer the iodine was left in contact with the reduced mixture before titrating with thiosulphate, the more iodine was reduced, and moreover, when the excess of iodine was titrated immediately after its addition, it required several tenths of a c.c. of  $N/10$  iodine solution to restore the blue colour to the starch indicator, showing that the

solution was still capable of reducing iodine. In fact, if the iodine solution was added very slowly, the addition of one c.c. was sometimes necessary before a permanent blue colour was obtained. On the other hand, where the iodine had been left in contact with the mixture for some hours before titration, only one drop of iodine was required to restore the blue colour. This time effect is due to a slow reduction of the iodine and not to any change within the mixture of dichromate and sulphurous acid, for some of this mixed solution, which had been left overnight without the addition of iodine, still showed the effect to about the same extent. The explanation of this curious behaviour will be given in the sequel.

When several c.c. of dilute sulphuric acid were added to the potassium dichromate or the sulphurous acid before the addition of the sulphurous acid or dichromate respectively, the amount of iodine which the mixture would reduce at once was the same as that reduced by the mixture of dichromate and sulphurous acid when left in contact with the iodine for several hours. If, however, the sulphuric acid was added after mixing the reagents, this effect became almost inappreciable. These results are summarised in the following table:

|   | Excess of<br>$\text{H}_2\text{SO}_3$ . | $\text{H}_2\text{SO}_3$<br>used up. | Mols. of<br>$\text{H}_2\text{SO}_3$ used<br>by 1 mol. of<br>$\text{K}_2\text{Cr}_2\text{O}_7$ . |
|---|--|-------------------------------------|---|
| a. 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine (titrated at once).....   | 0.0645 gram                            | 0.2207 gram                         | 3.24  |
| b. 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine (mixed, and left overnight before titrating) .....              | 0.0687 "                               | 0.2165 "                            | 3.18  |
| c. 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. $N/10\text{-H}_2\text{SO}_4$ + 50 c.c. iodine (titrated at once) ..... | 0.0657 "                               | 0.2195 "                            | 3.22  |
| d. 50 c.c. $N/10\text{-H}_2\text{SO}_4$ + 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine (titrated at once) ..... | 0.0687 "                               | 0.2165 "                            | 3.18  |
| e. 50 c.c. $N/10\text{-H}_2\text{SO}_4$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 c.c. iodine (titrated at once) ..... | 0.0691 "                               | 0.2161 "                            | 3.17  |

Moreover, in experiments (d) and (e), one drop of iodine was sufficient to restore the blue colour of the mixture, hence we may conclude that the amount of sulphurous acid used in experiments (b), (d), and (e) represents the amount of sulphurous acid oxidised by 0.245 gram of potassium dichromate, and that consequently about 6 per cent. of dithionate is formed, since only 0.2044 gram of the acid would be oxidised if sulphate alone were produced. In another series of com-

parable experiments, about 5 per cent. of dithionate was formed; the quantity apparently varied from 4.5 to 6 per cent., similar quantities being produced when the sulphurous acid was prepared and kept in the dark. Hydrochloric acid was found to have the same effect as sulphuric acid.

Further experiments showed that when sulphuric acid is added to the dichromate its reactions are masked. Thus, to 5 c.c. of  $K_2Cr_2O_7$  ( $=0.1225$  gram  $K_2Cr_2O_7$ ) were added 10, 25, and even 50 c.c. of  $N/10-H_2SO_4$ , followed by 5 c.c. of  $H_2SO_3$  ( $=0.140$  gram  $H_2SO_3$ ); 25 c.c. of weak hydrochloric acid (about 1.6  $N$ ) were then introduced and the mixture at once tested with barium chloride. The green solution, which remained perfectly clear for several minutes, then became cloudy and a precipitate rapidly formed, whereas the same amounts of sulphuric and hydrochloric acids made up to the same volume gave an immediate precipitate with barium chloride.

If the sulphuric acid was added after the sulphurous acid, its reactions were masked in the same way. If hydrochloric acid is not added before testing with barium chloride, the solutions must be diluted to about 1/250th normal with regard to sulphuric acid, otherwise a precipitate is obtained immediately. In the case of solutions which contain large amounts of added sulphuric acid, it is, however, difficult to prevent the immediate formation of a precipitate with barium chloride without adding some hydrochloric acid. Potassium sulphate was also taken up in the same way as sulphuric acid, so that it gave no precipitate with barium chloride when tested in the manner indicated, but this did not affect the amount of iodine reduced.

Since the freshly reduced green solutions do not give the reactions of chromium or  $SO_4$  ions, but only those of potassium, it seems highly probable that the solutions contain  $\frac{KSO_3}{KSO_4} > Cr_2(SO_4)_2$ , formed as an intermediate compound when potassium dichromate is reduced. This compound, which is analogous to the chromosulphates prepared and investigated by Recoura (*Compt. rend.*, 1892, 114, 477), is the potassium salt of a complex chromosulphuric acid, and consequently its freshly prepared solution would not give the reactions of chromium or  $SO_4$  ions. The compound, however, slowly decomposes into potassium sulphite and chromium sulphate, which then give the usual reactions with ammonia and barium chloride.

If the green solutions employed are moderately concentrated, a precipitate, probably consisting of barium chromosulphate, is always obtained with barium chloride in the cold (see Recoura, *loc. cit.*), but the presence of hydrochloric acid prevents its formation.

The compound  $\frac{KSO_3}{KSO_4} > Cr_2(SO_4)_2$  would be partly a complex sulphite,



and it is very probable that this compound would not reduce iodine so quickly as an ordinary simple sulphite such as  $\text{K}_2\text{SO}_3$ , hence the effect of time on the amount of iodine reduced by the green solution, whereas no such time effect could be observed in the reduction of iodine by potassium sulphite.

The addition of sulphuric or hydrochloric acid to the dichromate solution probably leads to the formation of the acid  $\text{HSO}_3 > \text{Cr}_2(\text{SO}_4)_2$ , which at once reduces iodine as indicated below, or, in the case of sulphuric acid, perhaps  $\text{KSO}_4 > \text{Cr}_2(\text{SO}_4)_2$  and free sulphurous acid are formed, for, as has been shown, the reactions of the added sulphuric acid are masked. When the sulphuric acid is added subsequently to the reduction of the dichromate, it does not eliminate the time effect on the reduction of the iodine, but yet its reactions are masked, hence it may be concluded that compounds such as  $\text{KSO}_3 > \text{Cr}_2(\text{HSO}_4) \cdot \text{SO}_4$  are formed analogous to the di-, tri-, and other poly-chromosulphuric acids prepared and investigated by Recoura (*Bull. Soc. chim.*, 1893, 9, 586; *Compt. rend.*, 1893, 116, 1367), who states (*Compt. rend.*, 1892, 114, 477) that chromosulphuric acids can be prepared by adding sulphuric acid to a solution of the green chromium sulphate. The reactions described above seem to take place in a somewhat similar manner. It may be mentioned here that when 25 c.c. of *N*/10 sulphuric acid have been added to 5 c.c. of potassium dichromate ( $= 0.1225$  gram  $\text{K}_2\text{Cr}_2\text{O}_7$ ), as in the experiment just described, sufficient acid is present to form Recoura's acid,  $(\text{HSO}_4)_6\text{Cr}_2$ , and it is not easy to see what becomes of the acid added and taken up in excess of this amount; the formation of pyrosulphuric acids, such as  $(\text{HS}_2\text{O}_7)_6\text{Cr}_2$ , seems improbable.

In the cases already mentioned, where the dark solutions containing excess of chromate or chromic acid behave in a very similar way to the green ones containing excess of sulphurous acid and do not give the reactions of chromium or  $\text{SO}_4$  ions, it seems reasonable to assume that a compound  $\text{HCrO}_4 > \text{Cr}_2(\text{SO}_4)_2$ ,\* or its potassium salt, exists, together with a certain amount of the salt  $\text{KSO}_3 > \text{Cr}_2(\text{SO}_4)_2$ , when sulphite is also present.

The influence of temperature on the oxidation of sulphurous acid by potassium dichromate was next investigated, and it was found that the same amount of dithionate was formed within the limits  $0^\circ$  and  $85^\circ$ .

\* Such compounds have been prepared by Recoura (*Bull. Soc. chim.*, 1897, 18, 934).

In the following experiments, the sulphurous acid was added slowly to the dichromate (or dichromate and sulphuric acid) at about 85°, and the iodine was introduced after cooling the mixture. The solution of dichromate, sulphurous acid, and iodine had the same concentrations as those employed in the experiments indicated in the preceding tables.

|  | Excess of<br>$\text{H}_2\text{SO}_3$ . | $\text{H}_2\text{SO}_3$<br>used up. | Mols. of<br>$\text{H}_2\text{SO}_3$ used<br>by 1 mol. of<br>$\text{K}_2\text{Cr}_2\text{O}_7$ . |
|--|--|-------------------------------------|---|
| 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine   | 0·0622 gram                            | 0·2230 gram                         | 3·27  |
| 50 c.c. $\text{N}/10\text{-H}_2\text{SO}_4$ + 10 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine | 0·0632 „                               | 0·2220 „                            | 3·25  |
|  | 0·0716 „                               | 0·2136 „                            | 3·14  |
|  | 0·0716 „                               | 0·2136 „                            | 3·14  |

In the next series of experiments, the dichromate (or dichromate and sulphuric acid) was cooled in ice before adding the sulphurous acid.

|   | Excess of<br>$\text{H}_2\text{SO}_3$ . | $\text{H}_2\text{SO}_3$<br>used up. | Mols. of<br>$\text{H}_2\text{SO}_3$ used<br>by 1 mol. of<br>$\text{K}_2\text{Cr}_2\text{O}_7$ . |
|---|--|-------------------------------------|---|
| 5 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ (= 0·1225 gram) + 10 c.c. $\text{H}_2\text{SO}_3$ (= 0·1056 gram) + 50 c.c. iodine (0·0873 normal) | 0·1021 gram                            | 0·1091 gram                         | 3·20  |
| 25 c.c. $\text{N}/10\text{-H}_2\text{SO}_4$ + 5 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c. iodine   | 0·1044 „                               | 0·1068 „                            | 3·14  |

In another experiment, 0·2763 gram of  $\text{H}_2\text{SO}_3$  was added to 20 c.c. of the dichromate solution (= 0·49 gram of  $\text{K}_2\text{Cr}_2\text{O}_7$ ); the unreduced dichromate, estimated by titration with ferrous ammonium sulphate, was found to be 0·177 gram of dichromate, showing that only 0·313 gram had been reduced. Now, as 0·2763 gram of sulphurous acid would reduce 0·331 gram of potassium dichromate if sulphate alone were formed, it will be seen that about 6 per cent. of dithionate has been produced, as in the other cases in which excess of sulphurous acid was employed. The addition of sulphuric acid to the dichromate before adding the sulphurous acid had no effect on the reaction.

As was to be expected, the same percentage of dithionate is formed whether sulphurous acid is oxidised by potassium chromate, by chromic acid, or by dichromate. In the experiments with potassium

chromate, the current of carbon dioxide in the mixing flask was replaced by a current of hydrogen, since the former gas converts the chromate into dichromate.

The solution of potassium chromate contained 0.2586 gram in 10 c.c., whilst the sulphurous acid had a concentration of 0.2684 gram  $\text{H}_2\text{SO}_3$  in 10 c.c., the iodine solution was 0.0696 normal.

|   | Excess of<br>$\text{H}_2\text{SO}_3$ . | $\text{H}_2\text{SO}_3$<br>used up. | Mols. of<br>$\text{H}_2\text{SO}_3$ used<br>by 2 mols. of<br>$\text{K}_2\text{CrO}_4$ . |
|---|--|-------------------------------------|---|
| 10 c.c. $\text{K}_2\text{CrO}_4$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 75 c.c. iodine (titrated at once) .....  | 0.0885 gram                            | 0.1799 gram                         | 3.29  |
| 10 c.c. $\text{K}_2\text{CrO}_4$ + 10 c.c. $\text{H}_2\text{SO}_3$ + 75 c.c. iodine (left overnight before titrating)..   | 0.0958 ,,                              | 0.1726 ,,                           | 3.16  |
| 10 c.c. $\text{K}_2\text{CrO}_4$ + 10 c.c. $\text{H}_2\text{SO}_3$ (= 0.2108 gram $\text{H}_2\text{SO}_3$ ) + 50 c.c. iodine (0.0964 normal) (left overnight before titrating). | 0.0368 ,,                              | 0.1740 ,,                           | 3.18  |

If only sulphate were formed, 2 mols. of potassium chromate would have oxidised 3 mols. of sulphurous acid. The same amount of dithionate was produced when excess of potassium chromate was used.

As shown by Berthier (*loc. cit.*), if sulphurous acid is added to excess of potassium chromate, a precipitate of the brown chromium hydroxide is obtained. If the solutions are weak, however, a dark brown solution results which deposits a brown precipitate on boiling. Dark brown solutions are also obtained when sulphurous acid is added to excess of potassium dichromate or chromic acid, but no precipitate is formed, even on boiling. If, however, some ammonia solution is added, a precipitate of brown chromium hydroxide is obtained either at once or on boiling. This difference in behaviour is simply due to the excess of potassium chromate acting as an alkali, for if solutions of potassium chromate and chrome alum are mixed, a similar precipitate of chromium hydroxide is produced.

In some similar experiments with chromic acid solutions, it was found that sulphuric acid had no influence on the amount of iodine reduced, and no time effect was observed. It would appear, therefore, that the acid  $\frac{\text{HSO}_3}{\text{HSO}_4} > \text{Cr}_2(\text{SO}_4)_2$  reduces iodine at once.

In the following experiments, 10 c.c. of the chromic acid and sulphurous acid solutions contain 0.165 and 0.2108 gram of their respective reagents; the iodine solution employed was 0.0964 normal.

0.165 gram of chromic acid should oxidise 0.203 gram of sulphurous acid to sulphate.



|  | Excess of<br>$\text{H}_2\text{SO}_3$ . | $\text{H}_2\text{SO}_3$<br>used up. | Mols. of<br>$\text{H}_2\text{SO}_3$ used<br>by 2 mols. of<br>$\text{CrO}_3$ . |
|--|--|-------------------------------------|---|
| 10 c.c. $\text{CrO}_3$ + 15 c.c. $\text{H}_2\text{SO}_3$ + 50 c.c.<br>iodine .....   | 0.1036 gram                            | 0.2126 gram                         | 3.14  |
| 50 c.c. $\text{N}/10\text{-H}_2\text{SO}_4$ + 10 c.c. $\text{CrO}_3$ + 15 c.c.<br>$\text{H}_2\text{SO}_3$ + 50 c.c. iodine ..... | 0.1035 ,,                              | 0.2127 ,,                           | 3.14  |

These solutions, to which sulphuric acid or potassium sulphate has been added, like the dichromate solutions, do not show the presence of the sulphate ion.

An experiment was performed in which 0.2126 gram of sulphurous acid was added to 10 c.c. of the chromic acid solution (that is, the exact quantity required to reduce that amount of chromic acid). The resulting green solution, when sufficiently diluted, did not give a precipitate with either barium chloride or sodium phosphate, so that it evidently contained Recoura's green chromium sulphate (*Bull. Soc. chim.*, 1892, 7, 200), which, whatever be its constitution, cannot contain  $\text{SO}_4$  ions.

A few experiments were made to ascertain whether the dithionate could be satisfactorily estimated gravimetrically. The reduced chromate solutions were precipitated with barium hydroxide, excess of which was removed by carbon dioxide. The filtrate from the precipitate was evaporated and the dithionate present converted into barium sulphate. The gelatinous nature of the precipitate, however, made it practically impossible to remove the dithionate completely by washing; the dithionate is probably present in the precipitate as a chromodithionate, and consequently these experiments were abandoned as being unsatisfactory. That dithionate is formed during the reaction is shown by the fact that the residue of barium dithionate gave the theoretical quantity of barium sulphate:

0.0372 gram  $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  gave 0.0265 gram  $\text{BaSO}_4$  (calculated, 0.0260 gram  $\text{BaSO}_4$ ).

### *Electrolytic Experiments.*

Some electrolytic experiments were tried with the reduced green solutions, which showed in a very clear way the character of the compounds in solution. A solution containing chromic acid reduced by a slight excess of sulphurous acid was electrolysed beneath weak sulphuric acid in the manner described in a previous paper (Donnan

and Bassett, *Trans.*, 1902, 81, 939). The current employed varied from 0.02—0.03 ampere, and gradually diminished during the experiment owing to the cathode becoming polarised by a slight deposit of chromium hydroxide.

On electrolysing the freshly reduced solution, both the cathode and anode boundaries moved up towards their respective electrodes to about the same extent (about 1.5 cm. in an hour), but the anode boundary was green while the cathode boundary was distinctly violet. After the reduced solution had been kept for four hours, another sample was electrolysed under precisely similar conditions, and in this case it was found that the violet cathode boundary moved up twice as fast as the green anode boundary.

Another portion of the reduced solution, after being kept overnight, was treated in the same way, and this time the violet cathode boundary was found to move upwards, whilst the green anode boundary remained practically stationary.

These three experiments, performed with the same reduced green solution under precisely similar conditions, show very clearly how the constitution of the substance in solution changes. The solution evidently contains a green negative complex ion (consisting of chromium and  $\text{SO}_4$ ) which travels towards the anode, and which gradually decomposes into violet positive ions and  $\text{SO}_4$  ions. Reduced potassium dichromate solutions behaved in the same way.

Similar experiments were tried with a chrome alum solution which had been rendered green by heating and then cooled down. Exactly similar results were obtained as with the reduced solutions, that is to say, a green boundary moved up towards the anode while a violet boundary approached the cathode. From this experiment, it seems highly probable that the green colour of chrome alum solutions which have been heated is due to the formation of chromosulphate. This probability is strengthened by the fact that chromosulphates can be prepared by heating the solid alums (Recoura, *Bull. Soc. chim.*, 1893, 9, 586).

#### SUMMARY OF RESULTS.

When potassium dichromate, potassium chromate, or chromic acid is reduced by sulphurous acid, 94—95 per cent. of sulphate is formed together with 5—6 per cent. of dithionate, the amount of the latter produced being independent of the temperature.

The freshly reduced solutions do not give the reactions of chromium or of  $\text{SO}_4$  ions, and appear to contain a compound  $\frac{\text{KSO}_3}{\text{KSO}_4} > \text{Cr}_2(\text{SO}_4)_2$  (or the corresponding acid), which slowly decomposes into  $\text{Cr}_2(\text{SO}_4)_3$  and

$K_2SO_4$ . If sulphuric acid or potassium sulphate is added to these solutions, the reactions of  $SO_4$  are not given by the resulting mixture. It seems possible that one molecule of chromium sulphate may mask the reaction of as many as six molecules of sulphuric acid.

Electrolytic experiments show that the green solutions contain a green anion which slowly decomposes into violet chromium cations and  $SO_4$  ions.

In conclusion, I wish to express my best thanks to Sir William Ramsay for advice and for the interest he has taken in these experiments.

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## LXXI.—*The Velocity and Mechanism of the Reaction between Potassium Ferricyanide and Potassium Iodide in Neutral Aqueous Solution.*

By F. G. DONNAN and R. LE ROSSIGNOL.

### *Introduction.*

WHEN potassium ferricyanide and potassium iodide react in neutral aqueous solution, potassium ferrocyanide and free iodine are gradually produced. Conversely, a solution of iodine in potassium iodide oxidises ferrocyanide to ferricyanide. In both cases, a definite state of equilibrium is attained, which may be expressed by the equation :

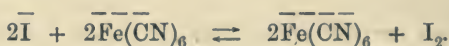


A rough preliminary experiment, in which the amount of free iodine (as  $I_2$  or  $\bar{I}_3$ ) was estimated by rapid titration of the cooled and diluted reaction mixture, showed that the equilibrium could be approached from either side. E. Rupp and A. Schiedt (*Ber.*, 1902, 35, 2430) have shown that potassium ferrocyanide can be estimated by oxidation to ferricyanide in presence of *excess* of iodine and titration of the excess of iodine by thiosulphate after a certain interval of time ( $\frac{1}{4}$ —1 hour). They make no mention, however, of the reversibility of the reaction in neutral solution. We have repeated some of these measurements and our attention was at once drawn to the existence of the reverse reaction, inasmuch as after the end-point with thiosulphate has been reached, free iodine soon reappears in the solution owing to interaction between the ferricyanide and the potass-

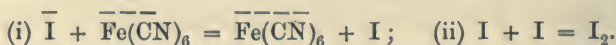


ium iodide. As shown in the present paper, however, the velocity of this reaction diminishes rapidly with decrease of the iodide concentration. Possibly, therefore, the reverse reaction escaped the attention of Rupp and Schiedt owing to the employment of less concentrated iodine solutions. The fact that practically complete oxidation of the ferrocyanide to ferricyanide can be obtained must be due to the excess of free iodine (as  $\bar{I}_3$ ) in the solutions employed.

Looking at the reaction from an ionic point of view, we may write it simply as follows, since all the salts occurring in the reaction are highly dissociated:



So far as the oxidation of potassium iodide by ferricyanide is concerned, it would be possible to express the mechanism of the reaction in a still simpler manner by dividing the main reaction into two successive ones:



On the plausible assumption that the second reaction occurs with immeasurably great speed, the oxidation of potassium iodide by ferricyanide might be regarded as a simple bimolecular reaction. It will be seen in the sequel, however, that such is very far from being the case.

In the following experiments, the order and course of this reaction have been investigated in order to gain some insight into the mechanism of the process. The disturbing effect due to the reverse reaction between iodine and potassium ferrocyanide has been avoided by adopting the method originally employed by Harcourt and Esson in their classical research on the speed of reaction, which consists in adding to the reacting mixture successive quantities of a solution of sodium thiosulphate and noting the times when free iodine makes its appearance as indicated by starch. In this way, the free iodine is removed as fast as it is formed, being, in fact, continually reconverted into ionic iodine. This method possesses also the great advantage that the concentration of the iodine ions does not alter to any appreciable extent during the reaction, so that in a given case the order of the reaction is determined solely by the number of the ferrocyanide ions taking part in the process.

#### *Method of Measurement.*

Equal volumes of solutions of potassium iodide and recrystallised potassium ferrocyanide, which had been previously brought to a constant temperature in the thermostat, were rapidly mixed and the time noted. A known quantity of sodium thiosulphate solution, correspond-

ing to about 10 per cent. of the total iodine liberated in the complete reaction, was immediately added together with a small amount of starch. As soon as the colour of the starch-iodine compound appeared, the time was noted and another similar quantity of thiosulphate solution introduced, this operation being repeated. In order to avoid any appreciable change in volume due to the successive quantities of thiosulphate solution added, the latter was employed in a very concentrated form, about 0.23 c.c. being added each time from a very small pipette. Preliminary experiments had shown that the amount added in this way was constant to one part in a thousand, provided that the pipette was rinsed each time into the reaction-mixture by sucking the latter up into the pipette once or twice. All the experiments recorded in this paper were carried out at a constant temperature of  $34.7^{\circ}$ . The Götze thermometer (divided into 1/10ths) employed in the thermostat was checked against a normal thermometer which had been calibrated by the Reichsanstalt.

#### *Experimental Results.*

The velocity of the reaction may be represented by an equation of the form

$$-dc_1/dt = kc_1^m c_2^n,$$

where  $c_1$  and  $c_2$  represent the concentrations of the ferricyanogen and iodine ions respectively, and  $m$  and  $n$  the number of these ions taking part in the reaction.

In the calculation of the velocity-constant, we have in general assumed the concentration of the ions to be proportional to the concentration of the dissolved salt. In the case of the potassium ferricyanide, this assumption can lead to no appreciable error, as the solutions employed were all very dilute ( $N/20$  to  $N/80$ ). The potassium iodide solutions employed were rather more concentrated ( $N/2$  to  $N/4$ ), owing to the slowness of the reaction in dilute solutions, but in this case a correction for varying ionisation has been introduced by means of the known values of the electrical conductivities obtained from Kohlrausch and Holborn's *Leitvermögen*. The investigation involved the determination of the exponents  $m$  and  $n$ .

#### *Determination of $m$ .*

In the following series of experiments, the concentration of the potassium iodide was in every case initially seminormal, and as this does not alter during the course of the reaction, the velocity equation takes the following form :

$$-dc_1/dt = (kc_2^n).c_1^m = Kc_1^m$$

where  $K = kc_2^n$ . The order of the reaction is therefore the same as  $m$ .

Since the total quantities of thiosulphate converted into tetrathionate are known for a certain number of intervals of time during the course of the reaction, the corresponding concentrations of ferricyanide can be calculated from the equivalent relationships  $\text{Na}_2\text{S}_2\text{O}_3 \equiv \text{I} \equiv \text{K}_3\text{Fe}(\text{CN})_6$ . In the following tables,  $c$  = concentration of ferricyanide (grams per litre),  $t$  = time (minutes).

TABLE I.

$c_0$  = Initial concentration of ferrocyanide =  $N/40$ .  
Constant concentration of potassium iodide =  $N/2$ .

| $c$ . | $t_1$ . | $m=1,$<br>$K=1/t \log c_0/c$ . | $t_m$ .   | $m=2, K=1/t(1/c-1/c_0)$ . |           |
|-------|---------|--------------------------------|-----------|---------------------------|-----------|
|       |         |                                |           | Expt. I.                  | Expt. II. |
| 7.425 | 4.72    | 0.0219                         | 4.75      | 0.00282                   | 0.00280   |
| 6.615 | 11.00   | 0.0198                         | 11.17     | 0.00271                   | 0.00267   |
| 5.803 | 18.97   | 0.0185                         | 19.18     | 0.00268                   | 0.00266   |
| 4.992 | 29.21   | 0.0171                         | 29.47     | 0.00270                   | 0.00268   |
| 4.180 | 43.18   | 0.0158                         | 43.51     | 0.00272                   | 0.00270   |
| 3.369 | 63.55   | 0.0149                         | 63.67     | 0.00275                   | 0.00275   |
|       |         |                                | Mean..... | 0.00273                   | 0.00271   |

In spite of a slight tendency to diminish to a minimum and then increase, the values of  $K$  calculated for  $m=2$  exhibit such a degree of constancy that the equation indicating a bimolecular reaction must be regarded as the appropriate one.

Experiments were now made in which the initial concentration of the potassium ferricyanide was varied, that of the potassium iodide being the same as before. The results are recorded in Tables II and III, where  $c$  and  $t$  have the same meanings as in Table I.

TABLE II.

$c_0$  = Initial concentration of ferricyanide =  $N/20$ .  
Constant concentration of potassium iodide =  $N/2$ .

| $c$ .  | $t$ . | $K=1/t(1/c-1/c_0)$ . |
|--------|-------|----------------------|
| 14.852 | 3.91  | 0.00169              |
| 13.230 | 9.70  | 0.00154              |
| 11.606 | 16.82 | 0.00153              |
| 9.984  | 26.00 | 0.00152              |
| 8.360  | 38.40 | 0.00151              |
| 6.738  | 58.40 | 0.00150              |
|        |       | Mean... 0.00156      |



TABLE III.

$c_0$  = Initial concentration of potassium ferricyanide =  $N/80$ .  
 Constant concentration of potassium iodide =  $N/2$ .

| $c$ . | $t$ . | $K = 1/t(1/c - 1/c_0)$ . |
|-------|-------|--------------------------|
| 3.713 | 5.55  | 0.00477                  |
| 3.307 | 12.77 | 0.00465                  |
| 2.901 | 21.87 | 0.00465                  |
| 2.496 | 33.70 | 0.00467                  |
| 2.090 | 49.75 | 0.00474                  |
| 1.684 | 73.00 | 0.00481                  |
|       |       | Mean... 0.00472          |

The results recorded in Tables I, II, and III exhibit a remarkable peculiarity. The value of the velocity-coefficient  $K$  appears to vary with the *initial* concentration of the potassium ferricyanide, becoming *greater* as the latter *diminishes*, as may be seen from the following summary of results :

|   |         |         |         |
|---|---------|---------|---------|
| Initial concentration of ferricyanide                         | $N/20$  | $N/40$  | $N/80$  |
| Value of $K$ (coefficient of the bi-molecular reaction) ..... | 0.00156 | 0.00272 | 0.00472 |

This variation of  $K$  cannot be ascribed either to varying ionisation or to any of the ordinary disturbing effects arising from the products of the reaction, since these would in general exert an influence during the course of the reaction, whereas the foregoing results show that the value of  $K$  is practically constant under these conditions. It is clear that this coefficient is affected by some factor which remains constant during a particular series of experiments, but which varies from one series to another. One such possible factor satisfying these conditions is the total concentration of ferrocyanogen *plus* ferricyanogen ions. Thus, in the reaction, the course of which is recorded in Table II, when the initial concentration of the ferricyanide was  $N/20$ , it is found that the value of the velocity-coefficient  $K$  is 0.00151, as calculated for a point when the reaction has proceeded to about 50 per cent., that is, when the concentration of the ferricyanide has fallen to about  $N/40$ , whereas on starting with an  $N/40$  solution of ferricyanide, as in Table I, the value 0.00281 is obtained for this constant. In the former case, however, the solution is  $N/40$  with respect to ferrocyanide, whilst in the latter it contains, initially, none of this salt. The value of the bimolecular reaction-coefficient appears at first sight to be lowered

by the presence of the ferrocyanide, but it is evident that it cannot be concluded that the ferrocyanide itself exercises a retarding influence on the velocity of the reaction, since this is not in accordance with the constancy of  $K$  during the course of any particular reaction. The only inference permissible, as far as the above results are concerned, is that the velocity-coefficient is a function of the total ferro- *plus* ferricyanogen concentration, and that this function increases with a decreasing value of the variable. This statement is confirmed by the following series of observations, the object of which was to ascertain the value of  $K$  in a case where the concentration of the reaction-mixture was initially  $N/40$  with respect to both ferro- and ferri-cyanides.

TABLE IV.

$c_0$  = Initial concentration of potassium ferricyanide or ferrocyanide =  $N/40$ .  
Constant concentration of potassium iodide =  $N/2$ .

| $c$ . | $t$ . | $K = 1/t(1/c - 1/c_0)$ . |
|-------|-------|--------------------------|
| 7.405 | 10.05 | 0.00135                  |
| 6.580 | 20.55 | 0.00149                  |
| 5.750 | 34.03 | 0.00154                  |
| 4.918 | 49.17 | 0.00167                  |
| 4.038 | 78.17 | 0.00158                  |
| 3.259 | 129   | 0.00144                  |
|       |       | Mean... 0.00151          |

Although the values of  $K$  exhibit a slight maximum, the mean, 0.00151, is in very close agreement with the mean value 0.00156, calculated in the case where the solution was initially  $N/20$  with respect to ferricyanide and contained initially no ferrocyanide (see Table II).

In both cases, the solution remained  $N/20$  throughout the course of the reaction with respect to ferricyanide *plus* ferrocyanide, and, in fact, the experiment recorded in Table IV may be regarded as a direct continuation of the former experiment (Table II).

Thus far, only a formal statement of the results of the experiments has been indicated; their interpretation is a more difficult matter. The reaction appears to be bimolecular with respect to the ferricyanogen ions, but the velocity-coefficient of this reaction appears to be a function of the total concentration of the complex iron-cyanogen ions. This phenomenon is conceivably connected with the effect of dilution on the stability of these complex ions, and a possible explanation of this interesting point is given on p. 713.

Under these circumstances, it does not appear justifiable to apply

any of the methods for determining the order of the reaction which are based on varying dilution, since these assume that the velocity-coefficient is intrinsically independent of concentration, whereas the course of the reaction may be disturbed by secondary causes. Thus the well-known formula

$$m = 1 + \log t_1/t_2 / \log c_2/c_1$$

is derived by integration from the differential velocity-equation

$$- dc/dt = kc^m$$

on the assumption that the velocity-coefficient  $k$  is independent of the concentration.\* As pointed out above, this assumption cannot be made in the present instance without certain reservations. Hence, in this case, the Noyes formula leads to erroneous results. If we apply it, for example, to the results given in Tables I and III, we obtain a value 1.2 for  $m$ , only slightly greater than unity. It would, however, be incorrect to conclude from this that the reaction is unimolecular with respect to the ferricyanogen ions.

#### *Determination of $n$ .*

As remarked before, the constant  $K$  involves the concentration of the potassium iodide in a manner expressed by the equation  $K = kc^n$ , where  $k$  is the intrinsic velocity-coefficient,  $c$  the concentration of iodine ions,  $n$  the number of iodine ions taking part in the reaction. Supposing that  $K_1$  and  $K_2$  are the values of  $K$  obtained in two experiments, in each of which the initial concentration of the ferricyanide is the same, whilst the concentrations of the potassium iodide are different, say  $c_1$  and  $c_2$ , the following equations are obtained :

$$K_1 = kc_1^n, \quad K_2 = kc_2^n,$$

whence  $n = \log K_1/K_2 / \log c_1/c_2$ .

It will be noted that it is necessary to start with the same initial concentration of ferricyanide in both cases, as otherwise the variation of  $K$  would be due to two causes. The measurements recorded in Tables V and VI were made with an initial concentration of ferricyanide equal to  $N/20$ , and may therefore be employed together with the results given in Table II for the purpose of determining the value of  $n$ .

\* This must not be confused with the fact that  $k$  is, for values of  $m > 1$ , a quantity, the numeric of which depends on the unit of concentration employed.



TABLE V.

Initial concentration of ferricyanide =  $N/20$  (16.475 grams per litre).  
 Concentration of potassium iodide =  $3/8N$  (62.25 „ „ ).

| $c.$  | $t.$  | $K = 1/t(1/c - 1/c_0).$ |
|-------|-------|-------------------------|
| 14.81 | 9.06  | 0.000750                |
| 13.16 | 21.71 | 0.000705                |
| 11.50 | 40.20 | 0.000652                |
| 9.837 | 62.75 | 0.000652                |
|       |       | Mean... 0.000689        |

TABLE VI.

Initial concentration of ferricyanide =  $N/20$  (16.475 grams per litre).  
 Concentration of potassium iodide =  $N/4$  (41.5 „ „ ).

| $c.$  | $t.$   | $K = 1/t(1/c - 1/c_0).$ |
|-------|--------|-------------------------|
| 14.81 | 27.50  | 0.000247                |
| 13.16 | 67.25  | 0.000227                |
| 11.50 | 118.70 | 0.000227                |
| 9.837 | 187.50 | 0.000218                |
| 8.179 | 279    | 0.000221                |
|       |        | Mean... 0.000228        |

On comparing Tables II, V, and VI, the following summary of results is obtained:

Concentration of potassium iodide (1)  $N/2$  (2)  $3/8N$  (3)  $1/4N$ .  
 Value of  $K$  ..... 0.00156 0.000689 0.000228.

It is evident that the value of  $K$  decreases rapidly as the concentration of the potassium iodide diminishes, which indicates a high value for the exponent  $n$ .

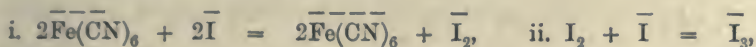
$$\begin{aligned}
 & \text{(Corrected for ionisation).} \\
 & 1 \text{ and } 2 \text{ give } n = \log \frac{0.00156}{0.000689} / \log \frac{4}{3} = 2.85 \quad 3.00 \\
 & 1 \text{ and } 3 \text{ give } n = \log \frac{0.00156}{0.000228} / \log 2 = 2.77 \quad 2.91 \\
 & 2 \text{ and } 3 \text{ give } n = \log \frac{0.000689}{0.000228} / \log \frac{3}{2} = 2.73 \quad 2.85
 \end{aligned}$$

If these numbers are corrected for the varying ionisation of the comparatively strong solutions of potassium iodide employed, as shown in the last column, they approach very closely to the value 3.

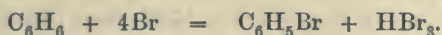
These results show that the velocity-coefficient  $K$  varies directly as the cube of the concentration of the iodine ions. This rather unexpected result points to the formation of complex  $\bar{I}_3$  ions in the primary reaction, and accordingly this change must be represented by the equation:



and not by the successive equations:



where the second equation represents a reaction which proceeds with very great speed in comparison with that represented by the first. Judging from the generally observed simplicity in the mechanism of chemical reactions, the latter hypothesis appeared to be more natural. It is, however, entirely negatived by the foregoing results. The primary formation of such complex halogen ions (or the corresponding undissociated compounds) has been already detected in kinetic investigations. Thus in the bromination of benzene in presence of iodine, L. Bruner (*Bull. Acad. Sci. Cracow*, 1902, 3, 195; *Abstr.*, 1902, ii, 447) found that the reaction was *quadrimolecular* with respect to bromine, according to the equation:



In an investigation of the action of bromine on alcohol in which the following change occurs,



S. Bugarswky (*Zeit. physikal. Chem.*, 1903, 42, 545) found it necessary to take into account the formation of  $\text{HBr}_3$  in the establishment of an equation to express the speed of the reaction.

Other investigations dealing with chemical equilibrium have conclusively proved the existence of complex  $\bar{I}_3$  ions in solution. The foregoing instances, together with the results obtained in the present investigation, indicate the primary part played by these complexes in the kinetics of chemical reaction. The question is a somewhat interesting and important one, for the results obtained indicate a more or less unexpected complexity in the mechanism of the process. Viewing the matter from the point of view of molecular kinetics, it seemed more natural to expect a primary reaction:



followed by an extremely rapid secondary change:  $I_2 + \bar{I} = \bar{I}_3$ , the latter, on account of its presumably great speed, being without influence on the velocity as measured experimentally.

The results obtained are, however, in accordance with another mode of viewing the question. Denoting the speed equations of the direct and inverse reactions by the formulæ:

$$v_1 = F_1 \text{ (direct : reaction between iodide and ferricyanide),}$$

$$v_2 = F_2 \text{ (inverse : reaction between iodine and ferrocyanide),}$$

where  $F_1$  and  $F_2$  denote the corresponding functions of the concentrations of the constituents involved, the equilibrium equation will be  $F_1 = F_2$ . Now this equation will undoubtedly involve the concentration of the  $\bar{I}_3$  ions. Hence the velocity-functions  $F_1$  and  $F_2$  will either explicitly contain the concentration of the  $\bar{I}_3$  ions or will involve the concentration of the iodine ions in such a manner as to include the formation of the complex iodine ions. These considerations are not interfered with in the present case by the fact that the  $\bar{I}_3$  ions are, on account of the method of measurement employed, at once reconverted into simple  $\bar{I}$  ions, for although this latter reaction occurs with very great speed, nevertheless the function  $F_1$  must necessarily involve the concentration of the iodine ions in the manner indicated, and it is this function the form of which is determined by the experimental measurements, since the reverse reaction is altogether eliminated by the method employed.

#### *The Effect of Dilution on the Velocity-Coefficient $K$ .*

The results of the present investigation indicate, therefore, the existence of a quinquemolecular reaction involving the primary and simultaneous interaction of two ferricyanogen and three iodine ions. This, at least, is the simplest and most direct interpretation of the results obtained in the determination of the exponents  $m$  and  $n$ . Unfortunately, however, the matter is not completely cleared up by this simple explanation, as there remains unexplained the peculiar variation of  $K$  in different series of experiments carried out with different initial concentrations of potassium ferricyanide. This question has already been briefly discussed on pp. 708—709, but no theory of the phenomenon was given, as it seemed desirable to present the results at first in a form which was free from any theoretical interpretation.



The following explanation has suggested itself to us as a possible one. Briefly summarised, the experiments have shown that, the concentration of the potassium iodide remaining always the same:

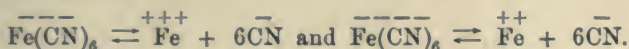
1. The velocity-coefficient is constant in any particular experiment with a given initial concentration of ferricyanide.

2. The velocity-coefficient is the same in different experiments with different initial concentrations of ferricyanide, provided the sum of the concentrations, ferricyanide *plus* ferrocyanide (expressed in terms of equivalent quantities), is the same in these experiments.

3. In different experiments in which the condition mentioned in 2 is not satisfied, the velocity-coefficient increases as the concentration sum, ferrocyanide *plus* ferricyanide, diminishes.

It may be assumed that in any particular experiment the sum of the concentrations of ferrocyanide and ferricyanide (which remains constant provided that concentrations are expressed in terms of equivalent quantities) is proportional to the sum of the concentrations of the ferro- and ferri-cyanogen ions, since the solutions were fairly dilute and the "strengths" of these ions are approximately the same.

Now, although the ions  $\overline{\text{Fe}(\text{CN})_6}$  and  $\overline{\text{Fe}(\text{CN})_6}$  are among the stablest of known complex ions, they must be to some extent dissociated in solution into their constituent simple ions in accordance with the equations:



If we denote the equivalent concentrations of the ferricyanogen, ferrocyanogen, ferric, and ferrous ions by the suffixes *ferric*, *ferroc*, *ferr*, *ferro*, respectively, the above equilibria correspond with the equations:

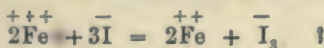
$$k_1 c_{\text{ferric}} = c_{\text{ferr}} c_{\text{CN}}^6 \quad \dots\dots\dots (i)$$

$$k_2 c_{\text{ferroc}} = c_{\text{ferro}} c_{\text{CN}}^6 \quad \dots\dots\dots (ii)$$

May it not be possible that it is the ferric ions which react with the iodine ions to form ferrous ions and free iodine, or rather  $\overline{\text{I}_3}$  ions, according to the equation:



or, in the case of formation of  $\overline{\text{I}_3}$  ions, the equation:



In the first place, this hypothesis would account for the comparative slowness of what appears to be a reaction depending on a simple

exchange of ionic charges, for the concentration of the ferric ions will at any moment be excessively small. In the second place, it can be shown that the above theory of the action leads, with the help of another simple and not improbable assumption, to a complete explanation of the experimental results. The assumption referred to consists in putting  $k_1 = k_2 = k$ , which means that the ferricyanogen and ferrocyanogen ions are dissociated to the same extent in solutions of equal equivalent concentrations, that is, that the complex ions in question are of practically equal stability.

According to this view, the mechanism of the reaction may be expressed as follows:

(a) The action,  $2\overline{\text{Fe}(\text{CN})_6} \rightarrow 2\text{Fe}^{+++} + 12\text{CN}^-$ , which occurs practically instantaneously, being a readjustment of a reversible ionic equilibrium disturbed by the removal of ferric ions.

(b) A change,  $2\text{Fe}^{+++} + 3\text{I}^- \rightarrow 2\text{Fe}^{++} + \text{I}_3^-$ , proceeding with measurable velocity.

(c) A combination,  $2\text{Fe}^{++} + 12\text{CN}^- \rightarrow 2\overline{\text{Fe}(\text{CN})_6}$ , taking place practically instantaneously, being a readjustment of a reversible ionic equilibrium disturbed by the addition of ferrous ions.

According to this view, the velocity-equation (for a constant concentration of iodide) must be written in the form:

$$-\frac{dc_{\text{ferric}}}{dt} = k'c_{\text{ferric}}^2.$$

But from the equilibrium-equation, (i)  $c_{\text{ferric}} = \frac{k}{c_{\text{CN}}^6} c_{\text{ferric}}$ ,

hence,

$$(ii) \quad -\frac{k}{c_{\text{CN}}^6} \frac{dc_{\text{ferric}}}{dt} = \frac{k'k^2}{c_{\text{CN}}^{12}} c_{\text{ferric}}^2$$

or (iii)  $-\frac{dc_{\text{ferric}}}{dt} = Kc_{\text{ferric}}^2$  where  $K = \frac{k'k}{c_{\text{CN}}^6}$ .

Equation (iii) corresponds in form with the equation already found to hold good, since the quantity of ferric ions present in the solution at any moment may be neglected in comparison with the amount of ferricyanogen ions.

The expression found for the velocity-coefficient  $K$  remains to be discussed. Considering the equations:

$$kc_{\text{ferric}} = c_{\text{ferric}} c_{\text{CN}}^6 \dots\dots\dots (ia),$$

$$kc_{\text{ferroc}} = c_{\text{ferroc}} c_{\text{CN}}^6 \dots\dots\dots (iia),$$

it is clear that at the end of the reaction, the concentration of the

cyanogen ions will be the same as at the beginning, since the amount resulting from the dissociation of the ferrocyanogen ions will equal that resulting from the dissociation of the ferricyanogen ions. Hence, the velocity-coefficient  $K$  will have the same value at the end as at the beginning. During the reaction, the value of  $c_{CN}$  will rise somewhat at first, since the number of cyanogen ions resulting from the ferrocyanogen ions produced will at first, owing to the dilution of the latter, be somewhat greater than the number which resulted previously from the corresponding ferricyanogen ions. Hence, the coefficient  $K$  will not remain absolutely constant, but will exhibit a minimum. It is noteworthy that the actual measurements show distinct signs of a minimum in the value of  $K$  (see, for example, Tables I and III).

The variation of coefficient  $K$  from one series of measurements to another now remains to be considered. Let  $a$  be the original total concentration of ferricyanogen ions in any series, and  $x$  the amount dissociated. Then the original concentrations of the ferric and cyanogen ions will be  $x$  and  $6x$  respectively, the equation of equilibrium being:

$$k(a-x) = x(6x)^6.$$

Since  $x$  is very small in comparison with  $a$ , we can write

$$ka = 6^6 x^7.$$

Hence,  $x$  will be proportional to  $\sqrt[7]{a}$ .

Accordingly,  $K$  will be inversely proportional to  $a^{\frac{1}{7}}$ , that is, to  $a^{0.143}$ . These results show that the velocity-coefficient  $K$  will increase as  $a$  diminishes, which agrees qualitatively with the experimental results. The exponent of  $a$  can be determined from the results tabulated on pp. 707—708.

$$\text{where } K_1 = \frac{k}{a_1^n}, \quad K_2 = \frac{k}{a_2^n};$$

$$\text{whence } \frac{K_2}{K_1} = \left(\frac{a_1}{a_2}\right)^n \text{ or } n = \log \frac{K_2}{K_1} / \log \frac{a_1}{a_2};$$

$$n = \log \frac{272}{156} / \log 2 = 0.80;$$

$$n = \log \frac{472}{272} / \log 2 = 0.79.$$

The exponent found experimentally is therefore 0.80, whereas the value deduced theoretically is 0.85. The agreement between these two numbers is remarkable, and affords a very important confirmation of the theory here proposed, which is thus seen to be capable of giving a quantitative description of the experimental results. The concentration of the ferric and ferrous ions must be extremely small, so small



in fact that the solubility products of the corresponding Prussian and Turnbull blues are not reached. Nevertheless, even these small amounts may be able to react with the iodine ions if the necessary time is allowed.

### *Summary of Results.*

1. The reaction between potassium ferricyanide and potassium iodide in neutral aqueous solution appears to be a *quinquemolecular* reaction, inasmuch as the velocity of the reaction is represented by the equation :

$$-\frac{dc_1}{dt} = kc_1^2c_2^3,$$

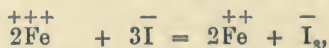
where  $c_1$  = concentration of ferricyanide,  $c_2$  = concentration of iodide.

2. The simplest interpretation of this result is that the reaction is represented by the equation :



3. This view of the matter does not, however, explain all the observed results, in particular, the variation of the velocity-coefficient with the total concentration, ferricyanide *plus* ferrocyanide.

4. If it is supposed that in reality the reaction occurs between ferric and iodine ions according to the equation :



the ferric ions resulting from the dissociation of the complex ferricyanogen ions, it can be shown that this theory supplies a complete quantitative account of all the observed results, provided that the not improbable assumption is made that the ferro- and ferri-cyanogen complexes are of equal stability.

In conclusion, we desire to take this opportunity of thanking Professor Ramsay for his interest and valuable advice during the course of this investigation.

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LXXII.—*The Action of Ammonia and Organic Bases on Ethyl Esters of Olefinedicarboxylic and Olefine- $\beta$ -ketocarboxylic Acids. Part II.*

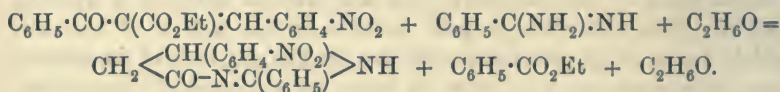
By SIEGFRIED RUHEMANN.

THE formation of olefine- $\beta$ -ketocarboxylic esters takes place by the action of hydrogen chloride, not only on the dry mixture of an aldehyde and a  $\beta$ -ketonic ester, but also, as I have found, on their solutions in alcohol or benzene. Thus, as shown below, ethyl *m*-nitrobenzylideneacetoacetate may readily be obtained in this manner. In some cases, this method may be found more convenient than that recommended by Knoevenagel (*Ber.*, 1896, 29, 172), since, on using primary or secondary amines as condensing agents, the condensation generally takes place in two directions, and yields either olefine- $\beta$ -ketonic esters or saturated diketonic esters, according to the temperature. For the preparation of members of the first class, the mixture has to be kept at a low temperature for several days, otherwise, the diketonic esters are formed. Knoevenagel and his pupils have established the fact that the amines differ in their action, inasmuch as they effect the condensation of the aldehyde with the ketonic ester to a varying extent. This difference is most marked in the action of aromatic aldehydes on ethyl benzoylacetate, for, in the presence of piperidine, the mixture becomes solid after 24 hours and yields ethyl benzylidenebenzoylacetate,  $C_6H_5 \cdot CO \cdot C(:CH \cdot C_6H_5) \cdot CO_2Et$ , not only at  $0^\circ$ , but also at the temperature of the room, whereas diethylamine acts much more slowly, the solid product, which, in this case also, is ethyl benzylidenebenzoylacetate, only separating after 4—5 days. On dissolving the residual oil in alcohol and allowing the solution to remain for several days, it yields a semi-solid mass of crystals which melt at  $115$ — $116^\circ$ ; on cooling, the fused product solidifies, and then does not melt until  $129$ — $130^\circ$ . The compound is ethyl benzylidenebisbenzoylacetate,  $C_6H_5 \cdot CH[CH(CO \cdot C_6H_5)CO_2Et]_2$ .

This result differs from Knoevenagel's observation (*Annalen*, 1894, 281, 55), according to which the mixture of ethyl benzoylacetate and benzaldehyde, when mixed with diethylamine and left for a long time in the cold, yields ethyl benzylidenebisbenzoylacetate, which melts at  $95^\circ$ . The melting point of the substance which I have obtained differs also from that of the product prepared by Curtius and Buchner (*Ber.*, 1885, 18, 2375) by the action of ethyl diazoacetate on benzaldehyde. This difference, however, may readily be explained if one takes into consideration Rabe's research on ethyl benzylidenebisacetoacetate (*Annalen*, 1900, 313, 129).

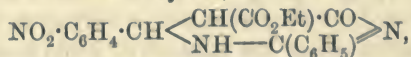
*m*-Nitrobenzaldehyde resembles benzaldehyde in its behaviour towards ethyl benzoylacetate. In the presence of piperidine, ethyl *m*-nitrobenzylidenebenzoylacetate is formed with the greatest ease, whilst on using diethylamine the reaction proceeds slowly, and finally yields ethyl *m*-nitrobenzylidenebisbenzoylacetate. According to Knoevenagel's researches, the diketonic esters are the result of the union between the olefine-ketonic esters first produced and the  $\beta$ -ketonic esters. The fact that the diketonic esters are formed with great ease from ethyl acetoacetate and aromatic aldehydes, whilst their formation takes place very slowly on using ethyl benzoylacetate, is most likely due to the stereochemical influence exercised by the phenyl group of ethyl benzoylacetate.

In my previous communication (Trans., 1903, 83, 374), I have shown that the condensation of ethyl benzylideneacetoacetate with benzamidine is accompanied by the removal of the acetyl group as ethyl acetate. The behaviour of the base towards ethyl *m*-nitrobenzylidenebenzoylacetate and ethyl *m*-nitrobenzylidenebenzoylacetate is analogous; in the one case, the acetyl group is eliminated as ethylacetate, whilst in the other, the benzoyl group is removed as ethyl benzoate; both olefine- $\beta$ -ketonic esters yield dihydro-*m*-nitrophenyl-phenylpyrimidone in accordance with the following equation :



However, on using ethyl benzylidenebenzoylacetate, I find that in its reaction with benzamidine only a part of the benzoyl group is removed with the formation of dihydrodiphenylpyrimidone and its benzoyl derivative,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}\left\langle\begin{array}{c} \text{CH}(\text{C}_6\text{H}_5) \\ \text{CO}\cdot\text{N}:\text{C}(\text{C}_6\text{H}_5) \end{array}\right\rangle\text{NH}$ .

The behaviour of benzamidine towards ethyl benzylidenemalonate (Ruhemann, Trans., 1903, 83, 376) is similar to that of the base towards ethyl *m*-nitrobenzylidenemalonate. Ethyl dihydro-*m*-nitrophenyl-phenylpyrimidonecarboxylate,



which is thus formed, on treatment with ammonia is transformed in the same way as ethyl dihydrodiphenylpyrimidonecarboxylate, and yields dihydro-*m*-nitrophenyl-phenylpyrimidone.



## EXPERIMENTAL.

*Action of Benzamidine on Ethyl m-Nitrobenzylideneacetoacetate.*

Ethyl *m*-nitrobenzylideneacetoacetate is readily prepared by saturating at 0° a concentrated solution of *m*-nitrobenzaldehyde and ethyl acetoacetate in alcohol, or, preferably, in benzene with hydrogen chloride. After remaining for 4—5 days at the ordinary temperature, the olefine-ketonic ester crystallises out. If alcohol is used as a solvent, the compound has a yellow colour, which can only be removed with difficulty; the ester, however, separates in almost colourless plates which melt at 110°, if the reaction takes place in a benzene solution, the yield is nearly quantitative:

0.2785 gave 13 c.c. moist nitrogen at 18° and 760 mm.  $N = 5.39$ .

$C_{13}H_{13}O_5N$  requires  $N = 5.32$  per cent.

This compound had been obtained before by Knoevenagel (*Ber.*, 1898, 31, 731) by gradually adding piperidine to an alcoholic solution of the aldehyde and ethyl acetoacetate, cooled by ice and salt, and allowing the mixture to remain in the cold for several days.

That a low temperature is necessary for the formation of the olefine-ketonic ester, if piperidine is used as a condensing agent, has been shown by Knoevenagel and Schürenberg (*Annalen*, 1898, 303, 223), for, at the ordinary temperature, they obtained in this way ethyl *m*-nitrobenzylidenebisacetoacetate. With the view of ascertaining whether the formation of this compound takes place with the same difficulty as that which I experienced in the preparation of ethyl benzylidenobisbenzoylacetate, I have repeated their experiment, and have arrived at the same result.

I find that the melting point of the substance is 148°, as compared with 146° recorded by these investigators:

0.2086 gave 0.4443  $CO_2$  and 0.1130  $H_2O$ .  $C = 58.08$ ;  $H = 6.01$ .

0.2963 „ 9.4 c.c. moist nitrogen at 19° and 754 mm.  $N = 3.61$ .

$C_{19}H_{23}O_8N$  requires  $C = 58.02$ ;  $H = 5.85$ ;  $N = 3.56$  per cent.

Benzamidine reacts with ethyl *m*-nitrobenzylideneacetoacetate in a similar manner and yields *dihydro-m-nitrophenyl-phenylpyrimidone*,  $CH_2 < \begin{smallmatrix} CH(C_6H_4 \cdot NO_2) \\ CO \cdot N : C(C_6H_5) \end{smallmatrix} > NH$ , with the loss of the acetyl group as ethyl acetate and the removal of alcohol. This product is soluble with difficulty in boiling alcohol, but does not separate from the solution until the latter is concentrated; it crystallises in colourless needles which melt at 192—193°:

0.2050 gave 0.4895  $\text{CO}_2$  and 0.0825  $\text{H}_2\text{O}$ .  $\text{C} = 65.05$ ;  $\text{H} = 4.46$ .

0.2030 „ 25 c.c. moist nitrogen at  $18^\circ$  and 761 mm.  $\text{N} = 14.23$ .

$\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_3$  requires  $\text{C} = 65.08$ ;  $\text{H} = 4.40$ ;  $\text{N} = 14.24$  per cent.

Dihydrodiphenylpyrimidone and its nitro-derivative are both insoluble in caustic potash and freely soluble in hydrochloric acid; the latter, however, differs from the former inasmuch as its solution in hydrochloric acid does not yield a precipitate with platinic chloride.

### *Action of Benzaldehyde on Ethyl Benzoylacetate.*

Ethyl benzylidenebenzoylacetate was first obtained according to Claisen's method by W. H. Perkin, jun. (Trans., 1885, 47, 260). As I have mentioned in the introduction, it may be prepared with the greatest ease by the action of amines on a mixture of benzaldehyde and ethyl benzoylacetate. This reaction has been previously studied by Knoevenagel (*loc. cit.*), who states that ethyl benzylidenebisbenzoylacetate melting at  $95^\circ$  is produced under the influence of diethylamine. The record of my experiments is as follows:

#### *(i) Piperidine used as Condensing Agent.*

Five to six drops of the base are added at the ordinary temperature to a mixture, in molecular proportions, of ethyl benzoylacetate (9.6 grams) and benzaldehyde (5.3 grams). When left overnight, the whole mass solidifies; the solid crystallises from alcohol in colourless needles melting at  $98-99^\circ$ . The same result is obtained on adding the base to a mixture of 5 grams of the ester and 1.5 grams of the aldehyde, which has been cooled down by ice. The melting point of the compound which is thus formed is identical with that observed by Perkin for ethyl benzylidenebenzoylacetate. The composition of the substance has been verified by the following analyses:

0.2033 gave 0.5750  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C} = 77.12$ ;  $\text{H} = 5.79$ .

0.2032 „ 0.5740  $\text{CO}_2$  „ 0.1048  $\text{H}_2\text{O}$ .  $\text{C} = 77.04$ ;  $\text{H} = 5.73$ .

$\text{C}_{18}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 77.14$ ;  $\text{H} = 5.71$  per cent.

#### *(ii) Diethylamine used as Condensing Agent.*

I have repeated Knoevenagel's experiment, and have found that after leaving the mixture for 4-5 days in ice-water a large crop of crystals separates. These, when separated from the residual oil and recrystallised from alcohol, melt at  $98-99^\circ$ . The melting point and

the following analysis prove the substance to be ethyl benzylidenebenzoylacetate :

0.2057 gave 0.5815  $\text{CO}_2$  and 0.1062  $\text{H}_2\text{O}$ .  $\text{C} = 77.08$  ;  $\text{H} = 5.73$ .

$\text{C}_{18}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 77.14$  ;  $\text{H} = 5.71$  per cent.

The alcoholic filtrate from this ester, after remaining for several days at the ordinary temperature, yields a semi-solid mass of colourless crystals. These dissolve readily in boiling alcohol and gradually separate from the cold solution in groups of small needles quite different from the long, shiny crystals of ethyl benzylidenebenzoylacetate. Whilst the latter melts at  $98-99^\circ$ , the former has the melting point  $115-116^\circ$ ; on cooling, it solidifies again and then melts at  $129-130^\circ$  :

0.2107 gave 0.5695  $\text{CO}_2$  and 0.1145  $\text{H}_2\text{O}$ .  $\text{C} = 73.71$  ;  $\text{H} = 6.03$ .

$\text{C}_{29}\text{H}_{28}\text{O}_6$  requires  $\text{C} = 73.72$  ;  $\text{H} = 5.93$  per cent.

Ethyl benzylidenebisbenzoylacetate is insoluble in solutions of the caustic alkalis, and its alcoholic solution does not give a coloration with ferric chloride. Curtius and Buchner (*loc. cit.*) have noticed that their ethyl benzylidenebisbenzoylacetate (m. p.  $103^\circ$ ) differs from ethyl benzylidenebenzoylacetate in its behaviour towards concentrated sulphuric acid. The same difference is noticed in the case of the ester (m. p.  $115-116^\circ$ ) which I have described ; this compound dissolves in the acid yielding a light yellow solution which, when heated, becomes yellowish-brown, whilst the solution of ethyl benzylidenebenzoylacetate in the acid is red and changes to light yellow on warming.

The olefine  $\beta$ -ketonic ester can be prevented from separating out, and the formation of ethyl benzylidenebenzoylacetate, only, can be effected, if the alcoholic solution of benzaldehyde, ethyl benzoylacetate, and diethylamine is allowed to remain at the ordinary temperature. The crystals which separate gradually increase in quantity, until after a fortnight the ethyl benzoylacetate has become almost entirely transformed. The product, after crystallisation from alcohol, melts at  $115-116^\circ$  and agrees also in its other properties with ethyl benzylidenebisbenzoylacetate.

#### *Action of Benzamidine on Ethyl Benzylidenebenzoylacetate.*

This reaction takes place when the ester is boiled with benzamidine hydrochloride and sodium ethoxide dissolved in absolute alcohol. After a short time, colourless crystals separate, and the odour of ethyl benzoate becomes perceptible. The heating is continued for about an hour, the alcohol distilled from the water-bath, and the solid which remains behind, washed with water and dilute alcohol. The product

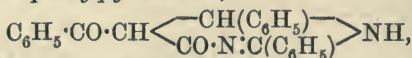


is a mixture of dihydrodiphenylpyrimidone and its benzoyl derivative; these substances are readily separated by cold hydrochloric acid, which dissolves the former with the greatest ease, leaving behind the benzoyl compound. The acid solution, when neutralised with caustic potash, yields a precipitate which crystallises from alcohol in colourless needles. The identity of this substance with dihydrodiphenylpyrimidone (Trans., 1903, 83, 376) follows from the melting point (180°) and the analysis:

0.2105 gave 20.6 c.c. moist nitrogen at 19° and 757 mm.  $N = 11.20$ .

$C_{16}H_{14}ON_2$  requires  $N = 11.20$  per cent.

*Dihydrobenzoyldiphenylpyrimidone,*



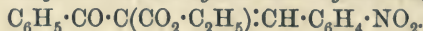
which remains undissolved in the hydrochloric acid, is only sparingly soluble in alcohol, but dissolves readily in boiling nitrobenzene and, on cooling, crystallises in colourless prisms which melt at 241—242° to a yellow liquid:

0.2015 gave 0.5752  $CO_2$  and 0.0950  $H_2O$ .  $C = 77.85$ ;  $H = 5.23$ .

0.2258 „ 15.6 c.c. moist nitrogen at 18° and 765 mm.  $N = 8.03$ .

$C_{23}H_{18}O_2N_2$  requires  $C = 77.96$ ;  $H = 5.08$ ;  $N = 7.91$  per cent.

*Ethyl m-Nitrobenzylidenebenzoylacetate,*



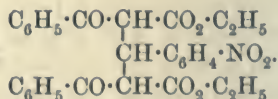
This ester may be obtained by saturating a solution of *m*-nitrobenzaldehyde and ethyl benzoylacetate at 0° with hydrogen chloride. After 2—3 weeks, colourless plates separate which melt at 107—108°. It is, however, more readily prepared by adding a small quantity of piperidine to the concentrated alcoholic solution of the aldehyde and ethyl benzoylacetate. When left overnight, the solution yields a semi-solid mass of crystals, which are recrystallised from alcohol:

0.2015 gave 0.4915  $CO_2$  and 0.0890  $H_2O$ .  $C = 66.52$ ;  $H = 4.90$ .

0.2252 „ 8.8 c.c. moist nitrogen at 21° and 756 mm.  $N = 4.42$ .

$C_{18}H_{15}O_5N$  requires  $C = 66.46$ ;  $H = 4.62$ ;  $N = 4.30$  per cent.

*Ethyl m-Nitrobenzylidenebisbenzoylacetate,*



If, instead of piperidine, diethylamine (6 drops) is added to the alcoholic solution of ethyl benzoylacetate (5 grams) and *m*-nitrobenz-

aldehyde (1.5 grams), a solid separates after 2—3 weeks, which crystallises from alcohol in colourless prisms melting at 128—129° :

0.2058 gave 0.5083 CO<sub>2</sub> and 0.0965 H<sub>2</sub>O. C = 67.36 ; H = 5.21.

0.2607 „ 6.2 c.c. moist nitrogen at 14° and 760 mm. N = 2.80.

C<sub>20</sub>H<sub>17</sub>O<sub>3</sub>N requires C = 67.31 ; H = 5.22 ; N = 2.70 per cent.

*Action of Benzamidine on Ethyl m-Nitrobenzylidenemalonate.*

In this condensation, dihydro-*m*-nitrophenyl-phenylpyrimidone is produced, being attended, as in the previous case (p. 721), by the elimination of the benzoyl group as ethyl benzoate. The identity of the product with the compound described above is proved by the melting point (192°) and the following nitrogen determination :

0.2068 gave 25 c.c. moist nitrogen at 17° and 764 mm. N = 14.10.

C<sub>16</sub>H<sub>13</sub>O<sub>3</sub>N<sub>3</sub> requires N = 14.24 per cent.

*Ethyl m-Nitrobenzylidenemalonate*, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH:C(CO<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.

This ester may be obtained according to Knoevenagel and Hoffmann's directions (*Ber.*, 1898, 31, 2593) for the preparation of ethyl *p*-nitrobenzylidenemalonate, namely, by digesting at 50° for 5—6 hours a mixture of *m*-nitrobenzaldehyde and ethyl malonate with a small quantity of piperidine; it is also formed at the ordinary temperature. After 1—2 days, the aldehyde dissolves in the mixture of the reagents, and the yellow solution slowly yields a deposit of crystals which gradually increase in quantity, until after 3 weeks, the whole mass has become solid. The product readily dissolves in boiling alcohol and, on cooling, crystallises in yellow plates melting at 75—76°. Stuart (*Trans.*, 1886, 49, 361), who previously described the ester, gave the melting point as 73° :

0.2390 gave 10 c.c. moist nitrogen at 16° and 764 mm. N = 4.90.

C<sub>14</sub>H<sub>15</sub>O<sub>6</sub>N requires N = 4.78 per cent.

*Ethyl Dihydro-m-nitrophenyl-phenylpyrimidonecarboxylate.*

The solution of ethyl *m*-nitrobenzylidenemalonate, benzamidine hydrochloride, and sodium ethoxide in absolute alcohol, when boiled on the water-bath, assumes a deep yellow colour and deposits a solid. After an hour's digestion, the mixture is cooled; the solid is collected and washed with water. The product dissolves in boiling alcohol with difficulty, and crystallises from the solution on cooling in colourless, silky needles which melt at 181—182° :

0.2098 gave 0.4785  $\text{CO}_2$  and 0.0888  $\text{H}_2\text{O}$ .  $\text{C} = 62.20$ ;  $\text{H} = 4.70$ .

0.2515 „ 24.6 c.c. moist nitrogen at  $13^\circ$  and 757 mm.  $\text{N} = 11.50$ .

$\text{C}_{19}\text{H}_{17}\text{O}_5\text{N}_3$  requires  $\text{C} = 62.12$ ;  $\text{H} = 4.63$ ;  $\text{N} = 11.44$  per cent.

On remaining in contact with an excess of strong aqueous ammonia for about a week, the ester almost completely dissolves, yielding a deep yellow solution; this, when concentrated on the water-bath, deposits a solid which crystallises from alcohol in colourless needles melting at  $192\text{--}193^\circ$ :

0.2405 gave 28.6 c.c. moist nitrogen at  $13^\circ$  and 769 mm.  $\text{N} = 14.22$ .

$\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}_3$  requires  $\text{N} = 14.24$  per cent.

The compound is therefore dihydro-*m*-nitrophenyl-phenylpyrimidone.

In conclusion, I may state that I am pursuing the research on the lines indicated in this paper.

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CAMBRIDGE.

### LXXIII.—*Note on the Formation of the Di- and Hexamethylammonio-cadmium Chlorides.*

By W. R. LANG, D.Sc.

WITH the view of determining whether compounds, similar to the ammonio-cadmium chlorides described in a former paper (Lang and Rigaut, *Trans.*, 1899, **84**, 883), were formed from dry liquid methylamine and anhydrous cadmium chloride, the author, in 1900, substituted methylamine for ammonia in the following experiments. Five grams of dry cadmium chloride were placed in a tube of hard glass immersed in solid carbon dioxide, and methylamine, obtained by warming a 12 per cent. solution of the base, and dried over solid caustic potash, was passed into the tube until the liquid was about one inch above the salt. At this temperature ( $-80^\circ$ ), no apparent action took place. The tube was then sealed and allowed to attain the ordinary temperature, when a violent reaction was observed, accompanied by considerable intumescence. In another experiment, the tube containing the salt was kept at  $-11^\circ$  when combination readily occurred. An excess of methylamine was employed to ensure the completion of the reaction, the tube being sealed and left overnight. The tube,



which was first immersed in carbon dioxide and then opened, was next transferred to melting ice and, after 3 hours, again sealed. Analysis of the resulting powdery substance gave :

$\text{CdCl}_2 = 49.1$  ;  $\text{CH}_3 \cdot \text{NH}_2 = 50.9$  ; whilst  $\text{CdCl}_2, 6\text{CH}_3 \cdot \text{NH}_2$  requires  $\text{CdCl}_2 = 49.57$  ;  $\text{CH}_3 \cdot \text{NH}_2 = 50.43$  per cent.

The composition of this compound corresponds exactly with the hexa-ammonio-compound obtained by Croft (*Phil. Mag.*, 1842, iii, 21, 355), and further described by Lang and Rigaut (*vide supra*).

A further portion was prepared, heated for 2 hours at  $100^\circ$ , and analysed :

Found  $\text{CdCl}_2 = 76.1$  ;  $\text{CH}_3 \cdot \text{NH}_2 = 23.9$ .

$\text{CdCl}_2, 2\text{CH}_3 \cdot \text{NH}_2$  requires  $\text{CdCl}_2 = 74.5$  ;  $\text{CH}_3 \cdot \text{NH}_2 = 25.3$  per cent.

This result indicates the existence of a very stable compound,  $\text{CdCl}_2, 2\text{CH}_3 \cdot \text{NH}_2$ . On heating still further, decomposition began at  $220^\circ$  and was not complete at  $300^\circ$ .

The author wishes to thank Mr. J. A. Russell Henderson, of Glasgow University, for assisting in these experiments.

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## LXXIV.—*The Relative Affinities of Polybasic Acids.*

By HARRY MEDFORTH DAWSON.

IF a solution of a soluble base is added to a solution containing two different acids, the quantity of which is more than sufficient to neutralise the base, then, if the system is homogeneous, it is well known that the base will distribute itself between the two competing acids in a ratio dependent on the specific nature of the acids and on their relative quantities. This ratio of distribution has been determined experimentally by several different methods. For the particular case where the two acids and the base are present in equivalent quantities, the experimentally determined ratio of distribution (corrected, if necessary, for secondary disturbances) expresses what J. Thomsen termed the relative avidities of the two acids. Numbers expressing the avidities of a large number of acids in terms of a standard acid have been calculated from the thermochemical volume and refractive

index measurements of Thomsen and Ostwald, and these numbers express the salt-forming powers of the respective acids relatively to that of the standard acid when the acids are present in equivalent proportions.

It is usual at the present day to denote the capacity of a substance to act as an acid by the term affinity. The relative affinities and the relative avidities of acids are generally assumed to be synonymous terms. According to modern views regarding the mode of action of an acid, a distinction should, however, be drawn between the two factors in the case of polybasic acids. On the basis of the theory of electrolytic dissociation, the strength or affinity of an acid in aqueous solution is determined by the concentration of hydrogen ions in the solution, and for comparable quantities of different acids dissolved in the same volume of water, the concentration of the hydrogen ions will be determined by the degree of dissociation of the acids. Respecting the quantities of different polybasic acids which are to be regarded as comparable in the above sense, attention must be paid to the mode of dissociation of the acids.

For weak polybasic acids, it is known that the electrolytic dissociation of hydrogen ions takes place in stages, one only of the acid hydrogen atoms being removed from the undissociated molecule in the first stage. When a state of dilution has been reached at which the first hydrogen ion is dissociated to a very considerable extent, then dissociation of a second hydrogen ion begins to take place. This dissociation in stages explains the fact that weak di- and tri-basic acids satisfy the dilution formula of Ostwald (deduced theoretically for monobasic acids) with the same degree of exactitude as monobasic acids provided the concentrations are not extremely small.

If, then, the character of the weak polybasic acids is such that at ordinary concentrations they dissociate in the same manner as monobasic acids, it follows that the quantities of the different acids which are comparable are molecular and not equivalent quantities. To determine directly the relative affinities of weak polybasic acids from their base-combining power, the quantities of the acids should be molecular.

For many polybasic acids, the dissociation tendencies, not only of the first hydrogen ion, but also of the second and the third, have been experimentally investigated.

The ionisation tendencies of the second and third hydrogen atoms obviously come into play in solutions of the acid salts of the types  $M'HX''$  and  $M'_2HX'''$ . Determinations of the concentration of the hydrogen ions in solutions containing such acid salts of di- and tri-basic acids have been carried out by Trevor (*Zeit. physikal. Chem.*, 1892, 10, 321) and W. A. Smith (*Zeit. physikal. Chem.*, 1898, 25,

144, and 193), the experimental method of procedure consisting in determining the rate of inversion of cane sugar at 100°.

I have utilised some of their data for the purpose of comparing the extents of the first and second stages of the hydrogen dissociation in the case of the following weak polybasic acids: tartaric, malic, succinic, and citric acids. These acids were employed by the author in the experimental development of a new method for determining the distribution of a base between two competing acids (Trans., 1902, 81, 512). The following table contains the percentage degree of dissociation of the first ( $\alpha$ ) and second ( $\alpha'$ ) hydrogen ions for solutions containing respectively one gram-molecule of the acid or one gram-molecule of the acid salt in four litres, this particular concentration being chosen as representing a mean value of the concentrations at which experiments on the distribution of a base between two acids have been carried out. The value of  $\alpha$  has been obtained from Ostwald's dilution formula, that of  $\alpha'$  by making use of the simple relationship brought to light by the experiments of Trevor and Smith, according to which the hydrogen dissociation of the acid salt is proportional to the dilution.

|                     | $100\alpha_4$ | $100\alpha'_4$ |
|---------------------|---------------|----------------|
| Tartaric acid ..... | 6.23          | 0.087          |
| Malic acid .....    | 3.97          | 0.022          |
| Succinic acid ..... | 1.63          | 0.005          |
| Citric acid .....   | 5.73          | 0.060          |

For the calculation of the values of  $\alpha'_4$ , the experimentally determined degree of dissociation of the acid salts at a dilution of 128 litres has been taken as a basis. Although the values of  $\alpha_4$  and  $\alpha'_4$  may not be very accurate, since, possibly, the dissociation formulæ employed no longer hold good for such a high concentration as 0.25 molecular, yet these numbers are sufficiently approximate to show the great difference in the extent of dissociation of the first and second hydrogen ions. The numbers indicate that for the four polybasic acids considered, the degree of hydrogen dissociation of the acid salt is only about 1 per cent. of that of the free acid when the concentration in each case is 0.25 molecular. If the dissociation of the second hydrogen ion takes place in a solution of the free acid, then, at the same molecular concentration, the value of  $\alpha'$  will be very much smaller on account of the considerable number of hydrogen ions already present in the solution as products of the primary dissociation. The molecule of a weak polybasic acid, in competing with a monobasic acid for a base, will therefore act as a molecule of a monobasic acid. In order to obtain directly from experiment the relative affinities of weak acids by measuring their base-combining powers, the quantities of the competing acids should therefore be in molecular ratio.



The case is different with strong polybasic acids as exemplified by sulphuric acid. For such acids in normal or one-tenth normal concentration, the dissociation of the second hydrogen ion is already very considerable. If we consider a solution containing equivalent quantities of hydrochloric and sulphuric acids, then theoretically we might suppose such a solution to contain three acids, namely, (1) hydrochloric acid, (2) sulphuric acid,  $\text{H}_2\text{SO}_4$ , giving rise to hydrogen ions by a primary dissociation process, and (3) the electrolytically charged acid  $\text{HSO}_4$ , also giving rise to hydrogen ions by further electrolytic dissociation. When the components of this solution compete for a base, which is supposed to be added to the solution in quantity insufficient for complete neutralisation, then the three substances,  $\text{NaCl}$ ,  $\text{NaHSO}_4$ , and  $\text{Na}_2\text{SO}_4$ , would result, and the quantities of these would be determined essentially by the respective degrees of hydrogen dissociation.

This view is only put forward as a simple way of looking at the partition phenomena in the case of strong polybasic acids. The theoretical development of the idea is rendered almost impossible by the fact that the dissociation laws for the strong acids (monobasic as well as polybasic) are as yet unknown, and further by the fact that the electrolytically charged acid, which is assumed here, is a dissociation product of the primary polybasic acid.

In the experimental determination of the partition ratio of a base between a strong monobasic and a strong polybasic acid by thermochemical and other measurements, the complicated behaviour of the polybasic acid in giving rise to acid salts as well as the normal salt has been corrected for by methods which are too well known to require repetition in this note. In such processes of correction, the neutral salt has been regarded as the normal product of salt formation. It may be noted, however, that in accordance with the above view the formation of the neutral salt of a polybasic acid of basicity  $n$  involves the replacement of  $n$  different hydrogen ions of very different dissociation tendencies, and such neutral salt formation is therefore a very complex phenomenon, involving as it does these  $n$  different factors.

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LXXV.—*The Chemical Dynamics of the Reactions between Chlorine and Benzene under the Influence of Different Catalytic Agents and of Light.*

By ARTHUR SLATOR, M.Sc., 1851 Exhibition Scholar of the University of Birmingham.

ALTHOUGH the whole series of chlorine substitution derivatives of benzene is known, only two addition compounds, namely,  $\alpha$ - and  $\beta$ -benzene hexachlorides, have been isolated. This result is in all probability due to the circumstance that an intermediate compound between benzene and benzene hexachloride, such as the di- or tetrachloride,  $C_6H_6Cl_2$  or  $C_6H_6Cl_4$ , would be unsaturated, and would therefore immediately react with chlorine.

It is probable that with a large excess of benzene only the two following reactions,  $C_6H_6 + Cl_2 = C_6H_5Cl + HCl$ ,  $C_6H_6 + 3Cl_2 = C_6H_6Cl_6$ , take place to any appreciable extent, the relative amounts of the products depending on the conditions of the experiment.

These reactions have been studied under various conditions, especially with regard to the effect of different catalytic agents, because in these changes a good example is afforded of the influence these substances may have on a reaction, both in accelerating its course and also in determining the relative amounts of the products and the values of the temperature-coefficient.

Page (*Annalen*, 1884, 225, 200), Willgerodt (*J. pr. Chem.*, [ii], 1886, 34, 264; 1887, 35, 391), and others have found that the chlorides and other compounds of many elements have a catalytic action in the above reactions, but in many cases the effect produced is not conveniently measured, and in this research the following substances have been employed: iodine chloride, tin tetrachloride, and ferric chloride; the accelerating effect of light upon the reaction has also been investigated.

The general method of measuring the velocity of reaction is as follows: a chlorine solution in dry benzene of suitable concentration (about 1/6-normal) is employed, and the reaction allowed to proceed under the influence of a catalytic agent, the rate of change being estimated by simultaneous titrations of chlorine and hydrogen chloride. The rate of disappearance of free chlorine is a measure of the sum of the velocities of both reactions, whilst the rate of formation of hydrogen chloride indicates the velocity of the substitution reaction. These measurements are controlled by an estimation of the amount of benzene hexachloride produced, this being effected by boiling with

excess of alcoholic sodium hydroxide, when the substance is decomposed quantitatively in accordance with the equation:  $C_6H_6Cl_6 = C_6H_5Cl_3 + 3HCl$ . The agreement between this estimation and the above titrations is satisfactory.

### *The Reaction without Catalytic Agents.*

The velocity of the reaction between chlorine and benzene without catalytic agents is exceedingly small, and it cannot be accurately measured with ordinary apparatus owing to the accelerating effect of small quantities of substances dissolved out of the glass.

### *Iodine Chloride as Catalytic Agent.*

With concentrations of iodine chloride varying from 1/150 to 1/400 gram-mol. per litre, the reaction proceeds at a convenient velocity. For the purpose of measuring the velocity with which free chlorine disappears in this and in the following experiments, the reaction was carried out in a vessel fitted at its lower end with a 3 c.c. pipette. A benzene solution of the catalytic agent (in this case iodine) was added to the chlorine solution, and from time to time 3 c.c. of the mixture were drawn off and titrated.

When the hydrogen chloride was simultaneously estimated, the experiments were carried out in sealed tubes or stoppered flasks in order to prevent the escape of the gas.

The chlorine was estimated by shaking with an aqueous solution of potassium iodide and titrating the iodine which is formed with neutral 1/50-normal sodium thiosulphate. The solution was subsequently titrated with 1/50-normal barium hydroxide in order to estimate the hydrogen chloride. Experiments carried out in this manner showed that iodine chloride has practically no action on benzene in the dark. These measurements show that the reaction is one of the first order with respect to the chlorine, the velocity of the reaction being proportional to the concentration of the chlorine present.

The values of  $K$ , calculated according to the formula  $K = \frac{1}{t} \log \frac{(Cl)t_0}{(Cl)t}$ , decrease slightly as indicated in Table I.\* To obtain comparable results, the mean value of  $K$  has been calculated for  $(Cl) = 10$  c.c. thiosulphate solution, that is, a 1/15-normal concentration of chlorine.

\* The concentration of a substance is expressed by enclosing its formula in brackets.



TABLE I.

Temp. 25°. Concentration of ICl = 0.00435 gram-mol. per litre.

| Time.  | Thiosulphate titre. | (Cl). | $K = \frac{1}{t} \log \frac{(Cl)_0}{(Cl)_t}$ |
|--------|---------------------|-------|--|
| 0 min. | 23.30               | 21.91 | —  |
| 5 "    | 21.10               | 19.71 | 0.0092                                       |
| 15 "   | 17.50               | 16.11 | 0.0089                                       |
| 30 "   | 13.50               | 12.11 | 0.0086                                       |
| 50 "   | 9.77                | 8.38  | 0.0084                                       |
| 80 "   | 6.34                | 4.95  | 0.0081                                       |
| ∞      | ICl = 1.39          | 0.00  | —  |

Mean [for (Cl) = 10 c.c.] = 0.0080

$$\frac{K}{(ICl)^2} \dots\dots\dots = 425.$$

TABLE II.

| Temperature. | ICl concentration. | K.      | $\frac{K}{(ICl)^2}$ |
|--------------|--------------------|---------|---------------------|
| 25°          | 0.00632            | 0.0167  | 420                 |
| "            | 0.00519            | 0.0115  | 430                 |
| "            | 0.00435            | 0.0080  | 425                 |
| "            | 0.00327            | 0.0046  | 430                 |
| "            | 0.00218            | 0.00208 | 440                 |
| 15°          | 0.00519            | 0.00109 | 405                 |
| "            | 0.00519            | 0.00107 | 400                 |
| 17°          | 0.00536            | 0.00114 | 400                 |

The velocity is therefore proportional to the square of the concentration of iodine chloride\* and the temperature coefficient of the reaction is very small.

When the hydrogen chloride was simultaneously titrated, it was found that only 70 per cent. of the reacting chlorine took part in the substitution reaction, whilst the remaining 30 per cent. disappeared to form the addition compound; this result was also confirmed by estimating the amount of benzene hexachloride produced.

\* L. Bruner (*Zeit. physikal. Chem.*, 1902, 41, 513) has investigated the dynamics of the bromination of benzene, and although the reaction is greatly complicated, owing to the retarding influence of the hydrogen bromide produced, yet the velocity "constants" obtained by him are approximately proportional to the square of the iodine concentration.

TABLE III.

| Titre of chlorine in<br>0·0192-normal<br>thiosulphate. | Titre of hydrogen<br>chloride in<br>0·0211-normal<br>barium hydroxide. | Percentage of chlorine<br>entering into the<br>substitution<br>reaction. |
|--|--|--|
| 19·23  | 5·85   | 67   |
| 28·03  | 8·95   | 70   |
| 32·63  | 10·42  | 70   |
| 37·09  | 12·20  | 72   |
| 31·60  | 10·20  | 71   |
| Mean.....  |  | 70   |

The distribution of the halogen between the two reactions remains constant for different concentrations of chlorine and iodine chloride, and is only slightly affected by temperature. This constancy indicates that addition and substitution are connected in such a manner that the velocity measured, which is the rate of disappearance of chlorine, is the velocity of a single reaction and not that due to two independent changes.

In repeating the above measurements with a mixture of carbon tetrachloride and benzene instead of benzene alone, it was found that the diluent caused a diminution in the velocity of the reaction owing to the decrease in the concentration of the benzene and also to the change of solvent, but the other factors, namely, the influence of the chlorine and iodine chloride concentrations, the slight decrease in the values of  $K$ , the small temperature-coefficient, and the distribution of the chlorine between the two reactions, remained as before. The following table summarises the results :

TABLE IV.

| Temperature. | Percentage<br>of benzene<br>by volume. | ICl concen-<br>tration. | $K$ .   | $\frac{K}{(ICl)^2}$ . |     |
|--------------|--|-------------------------|---------|-----------------------|-----|
| 25°          | 100                                    | see Table II            | —       | —                     | 430 |
| 15°          | "                                      | "                       | —       | —                     | 405 |
| 25°          | 50                                     | 0·00856                 | 0·0069  | 94                    | 99  |
| "            | "                                      | "                       | 0·0072  | 98                    |     |
| "            | "                                      | 0·00607                 | 0·0041  | 111                   |     |
| "            | "                                      | 0·00966                 | 0·0090  | 96                    |     |
| "            | "                                      | 0·01075                 | 0·0109  | 94                    |     |
| "            | 20                                     | 0·0105                  | 0·0031  | 28                    | 29  |
| "            | "                                      | 0·0147                  | 0·0062  | 29                    |     |
| "            | "                                      | 0·0172                  | 0·0088  | 30                    |     |
| 15°          | "                                      | 0·0174                  | 0·0088  | 29                    | 29  |
| "            | "                                      | 0·0135                  | 0·00535 | 29                    |     |
| 25°          | 10                                     | 0·0238                  | 0·0085  | 15                    | 15  |
| "            | "                                      | 0·0210                  | 0·0065  | 15                    |     |

The approximate doubling of the value  $\frac{K}{(\text{ICl})^2}$  when the concentration of the benzene is increased from 10 to 20 per cent. and the solvent changes only slightly shows that the velocity of reaction is proportional to the concentration of the benzene.

With the aid of the usual notation of chemical dynamics, the results can be summarised in the following equations:

$$-\frac{d(\text{Cl})}{dt} = K \cdot (\text{Cl}_2)(\text{C}_6\text{H}_6)(\text{ICl})^2; \quad \frac{K_{t+10}}{K_t} = 1.05.$$

If  $(\text{Cl})_s$ ,  $(\text{Cl})_a$  represent the amounts of chlorine which disappear in the substitution and addition reactions respectively, then the expression  $\frac{(\text{Cl})_s}{(\text{Cl})_s + (\text{Cl})_a} = 0.70$  is obtained.

*Tin Tetrachloride as Catalytic Agent.*—With this agent, the substitution reaction alone takes place. Half the chlorine appears as hydrogen chloride and no benzene hexachloride can be detected in the solution. As before, the reaction proceeds as one of the first order with respect to chlorine, and in this case without diminution in the values of  $K$ .

TABLE V.

| Time.      | Thiosulphate titre = (Cl). | $K = \frac{1}{t} \log \frac{(\text{Cl})_{t_0}}{(\text{Cl})_t}$ |
|------------|----------------------------|--|
| 0 min.     | 19.45                      | —  |
| 5 "        | 16.55                      | 0.0140   |
| 10 "       | 14.14                      | 0.0139   |
| 15 "       | 12.03                      | 0.0139   |
| 25 "       | 8.67                       | 0.0140   |
| 35 "       | 6.28                       | 0.0140   |
| 45 "       | 4.60                       | 0.0139   |
| 60 "       | 2.90                       | 0.0138   |
| 80 "       | 1.50                       | 0.0139   |
| 110 "      | 0.60                       | 0.0137   |
| $\infty$ " | 0.00                       | —  |
|            |                            | 0.0139   |

The velocity is proportional to the concentration of the tin tetrachloride and the temperature-coefficient is about 1.5.

TABLE VI.

| Relative concentration of $\text{SnCl}_4$ . | $K$ .   | $K \times 10^4$<br>$(\text{SnCl}_4)$ |
|---|---------|--------------------------------------|
| 4.00  | 0.0139  | 34.8                                 |
| 3.00  | 0.0106  | 35.3                                 |
| 2.00  | 0.00695 | 34.8                                 |
| 1.07  | 0.00380 | 35.5                                 |



TABLE VI.—(continued.)

| Temperature.  | K.  | Temperature-coefficient. |
|---|---|--------------------------|
| $\left\{ \begin{array}{l} 25^{\circ} \\ 15^{\circ} \end{array} \right.$ | $\begin{array}{l} 0.0073 \\ 0.0047 \end{array}$ | 1.55                     |
| $\left\{ \begin{array}{l} 25^{\circ} \\ 15^{\circ} \end{array} \right.$ | $\begin{array}{l} 0.0175 \\ 0.0119 \end{array}$ | 1.47                     |
|   |   | Mean..... 1.51           |

The results can be thus summarised :

$$-\frac{d(\text{Cl})}{dt} = K \cdot (\text{Cl}_2)(\text{SnCl}_4), \quad \frac{K_{t+10}}{K_t} = 1.5, \quad \frac{(\text{Cl})_s}{(\text{Cl})_s + (\text{Cl})_A} = 1.00.$$

*Ferric Chloride as Catalytic Agent.*—In this case also, substitution alone occurs. Accurate measurements of the velocity are rendered difficult owing to the disturbing effect of traces of moisture. The velocity was found to be proportional to the chlorine concentration and also to that of the ferric chloride.

TABLE VII.

| Concentration of ferric chloride = 1. |                     |        | Concentration of ferric chloride = 2. |                     |        |
|---------------------------------------|---------------------|--------|---------------------------------------|---------------------|--------|
| Time.                                 | Thiosulphate titre. | K.     | Time.                                 | Thiosulphate titre. | K.     |
| 0                                     | 20.84               | —      | 0                                     | 19.09               | —      |
| 10                                    | 19.30               | 0.0033 | 10.5                                  | 16.30               | 0.0068 |
| 25                                    | 17.50               | 0.0030 | 25                                    | 13.25               | 0.0064 |
| 45                                    | 15.55               | 0.0028 | 45                                    | 10.21               | 0.0060 |
| 90                                    | 12.16               | 0.0026 | 70                                    | 7.90                | 0.0055 |
| 165                                   | 8.40                | 0.0023 | $\infty$                              | 0.00                | —      |
| $\infty$                              | 0.00                | —      |                                       |                     |        |

The temperature-coefficient is large, and approaches the average value obtained for reactions in aqueous solution.

| Temperature.  | K.  | $\frac{K_{t+10}}{K_t}$ . |
|---|---|--------------------------|
| $\left\{ \begin{array}{l} 25^{\circ} \\ 16^{\circ} \end{array} \right.$ | $\begin{array}{l} 0.0117 \\ 0.0045 \end{array}$ | 2.7.                     |
| $\left\{ \begin{array}{l} 25^{\circ} \\ 16^{\circ} \end{array} \right.$ | $\begin{array}{l} 0.0073 \\ 0.0033 \end{array}$ | 2.3.                     |
|   |   | 2.5                      |

The results may be summarised in the equations :

$$-\frac{d(\text{Cl})}{dt} = K \cdot (\text{Cl}_2)(\text{FeCl}_3); \quad \frac{K_{t+10}}{K_t} = 2.5; \quad \frac{(\text{Cl})_s}{(\text{Cl})_s + (\text{Cl})_A} = 1.00$$

*A Mixture of Iodine Chloride and Tin Tetrachloride.*—The velocity of disappearance of free chlorine under the influence of a mixture of iodine chloride and tin tetrachloride was also measured and was found to be almost exactly equal to the sum of the velocities due to each catalytic agent separately. The diminution in the value of  $K$  which was observed in the catalysis effected by iodine chloride alone was not noticeable under these conditions, and there does not seem to be any reaction between the iodine chloride and tin tetrachloride.

$$K_{\text{SnCl}_4} = 0.0058.$$

$$K_{\text{ICl}} = 0.0045 \text{ (Cl} = 10 \text{ c.c.)}.$$

| Time.    | Thiosulphate titre. | (Cl). | $K = \frac{1}{t} \log \frac{(\text{Cl})_{t_0}}{(\text{Cl})_t}$ |
|----------|---------------------|-------|--|
| 0        | 30.60               | 29.50 | —  |
| 4.9      | 27.02               | 25.92 | 0.0112   |
| 15       | 21.20               | 20.10 | 0.0111   |
| 30       | 14.90               | 13.80 | 0.0110   |
| 50       | 9.00                | 7.90  | 0.0114   |
| 80       | 4.49                | 3.39  | 0.0117   |
| $\infty$ | 1.10                | 0.00  | —  |

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$$K_{(\text{SnCl}_4 + \text{ICl})} = 0.0113$$


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$$K_{\text{SnCl}_4} + K_{\text{ICl}} = 0.0103$$

#### *The Reaction under the Influence of Light.*

When chlorine interacts with benzene in the presence of light, no hydrochloric acid is formed, and accordingly addition only takes place (*Zeit. physikal. Chem.*, 1902, 41, 1). I have endeavoured to measure the velocity of this reaction in exactly the same way as that in which Goldberg determined the oxidation of quinine by chromic acid under the influence of light.

Tubes containing benzene and chlorine were exposed under similar conditions to diffused daylight, and from the velocity of the disappearance of free chlorine when the concentration of the halogen was varied in different tubes the apparent order of reaction was ascertained with respect to chlorine. When this order of reaction was corrected for light absorbed (the correction in extreme cases may amount to a whole unit), the true order of reaction was obtained, namely, that due to the influence of the concentration of chlorine on the velocity when the intensity of light is the same in each solution. The apparent order of reaction obtained by working with tubes 0.7 cm. wide was 1.2 to 1.4, and, when corrected for light absorbed, the reaction was found to be of the second order, within the limits of experimental error.

I have also measured the influence of the benzene concentration on the velocity. Equal concentrations of chlorine in 10 and 20 per cent. solutions of benzene in carbon tetrachloride were exposed to direct sunlight, and it was found that the chlorine disappeared approximately twice as fast in the 20 per cent. as in the 10 per cent. solution; hence, the velocity is proportional to the concentration of the benzene.

The temperature-coefficient of this reaction is comparatively large, being almost the same as in the case of the interaction with tin tetrachloride as catalyser, namely, 1.5 for 10°; this is contrary to the general rule for changes effected under the influence of light.

The results may be summarised in the following equations:

$$-\frac{d(\text{Cl})}{dt} = K \cdot (\text{Cl}_2)^2 \cdot (\text{C}_6\text{H}_6); \quad \frac{K_{t+10}}{K_t} = 1.5; \quad \frac{(\text{Cl})_A}{(\text{Cl})_A + (\text{Cl})_S} = 1.00.$$

In conclusion, I take the opportunity of thanking Professor Ostwald and his assistants for the interest they have taken in the progress of this investigation. I wish especially to express my gratitude and thanks to Dr. Luther for suggesting the subject of the research, and for the valuable advice and many kindnesses which I have received from him.

PHYSIKALISCH-CHEMISCHES INSTITUT,  
LEIPZIG.

## LXXVI.—*The Conditions of Decomposition of Ammonium Nitrite.*

By VICTOR HERBERT VELEY.

THE decomposition of ammonium nitrite in aqueous solution has for many years attracted the attention of investigators owing to its simplicity and to the readiness with which the nitrogen gas can be evolved and collected, and the undecomposed nitrite estimated.

Millon (*Ann. Chim. Phys.*, 1847, iii, 19, 255) noticed that a solution of ammonium nitrite can be preserved for several hours at the temperature of boiling water without decomposition if a drop of ammonia solution is added, but the addition of a drop of nitric, hydrochloric, or sulphuric acid produces "une effervescence vive et tumultueuse."

Later, Sorensen (*Zeit. anorg. Chem.*, 1894, 7, 38) made the remarkable observation that large masses of crystalline ammonium nitrite could be made spontaneously explosive by the addition of a trace of tartaric acid, but could be preserved for a month by the addition of a trace of ammonium carbonate. Wegscheider (*Zeit. physikal. Chem.*,



1901, 36, 543) has shown that, on the assumption of an ionic reaction,  $\text{NH}_4^+ + \text{NO}_2^- = 2\text{H}_2\text{O} + \text{N}_2$ , the addition of the ionic equivalent of salts produces the same acceleration.

Angeli and Boeris (*Atti Real. Accad. Lincei*, 1892, [ii], 1, 870) found that the addition of ammonium salts, on the one hand, and of nitrites, on the other, increases the rate of decomposition, whilst indifferent or neutral salts have no marked influence.

A more recent publication by Arndt (*Zeit. physikal. Chem.*, 1901, 39, 1), induced me to revert to a subject on which I made certain observations some years ago (*Phil. Trans.*, 1888, Series A., 179, 257), as some of his results were in accordance, whilst others were apparently discrepant, with my former work.

While the present investigation was in progress, Blanchard (*Zeit. physikal. Chem.*, 1902, 41, 680) studied the reaction with the view of ascertaining, firstly, which substances act as accelerators, and, secondly, whether subsidiary reactions do not modify the course of the reaction. As regards the first point, this author showed that the action of various acids could be expressed in terms of the ionic equation :

$$V = k(aC_{\text{H}} + bC_{\text{HNO}_2}) + C_{\text{NH}_4} + C_{\text{NO}_2},$$

in which  $V$  is the velocity, and  $k$ , and  $C$  have the usual significance.

As regards the second point, it was proved that there was no evidence of the evolution of oxides of nitrogen unless the reaction was modified by the addition of acid.

These various observations will be alluded to in the sequel, in so far as they have reference to the present inquiry.

#### *Preparation of Solutions of Ammonium Nitrite.*

For this purpose, the reaction between ammonium chloride and silver nitrite was selected; the latter salt was obtained by precipitating purified silver nitrate with sodium nitrite, washing the precipitate of silver nitrite three or four times with cold water, recrystallising from hot water, drying the crystals, first by suction, and then on a porous plate; all the operations were conducted in such a manner as to avoid as far as possible either contact with organic matter or exposure to direct sunlight. Weighed amounts of the silver nitrite thus prepared were decomposed with equivalent proportions of ammonium chloride in the presence of a small volume of water, the silver chloride filtered off, and the solution, when freed from all turbidity, made up to a known volume.

The concentration of the solution at the outset was determined by a decinormal solution of potassium permanganate, but in any continuous series of observations, the amount of ammonium nitrite undecomposed

was calculated from the evolved volume of nitrogen, corrected to standard pressure and temperature; this latter method is not of the same order of accuracy, as a certain quantity of nitrogen remains in the solution, but it was sufficiently approximate in cases in which the series of observations could not be interrupted.

The acidity or alkalinity of the solutions was determined by very dilute standard solutions of ammonia or sulphuric acid respectively, litmus being used as an indicator.

### *Method of Working.*

The ammonium nitrite solutions were placed in distillation flasks of 75 to 90 c.c. capacity, the volume used being such that when the thermometer was introduced, and the contents heated to the required temperature, the level of the liquid was nearly up to the side-delivery tube, and thus evaporation from a large surface avoided. My experience, however, coincided with that of Arndt, which was that the water formed by the reaction approximately counterbalanced the loss by evaporation. The flasks were closed with rubber plugs through which the thermometer passed, and the side limb connected by stout rubber tubing with a capillary tube drawn out so as to deliver small bubbles (about 75 per c.c.) of nitrogen. In most experiments, a standard volume of 4 to 5 c.c. was collected for each observation; if the evolution of gas was more rapid, 10 c.c., if less rapid, then 2 and even 1 c.c. of gas were collected.

In all cases,  $V/T$  represents volume of gas in c.c. collected in time expressed in minutes.

Three thermometers were used, all graduated in one-tenths of a degree, two of these instruments ranged from  $50^{\circ}$  to  $103^{\circ}$ , and one from  $0^{\circ}$  to  $20^{\circ}$ ; one of the former ( $1^{\circ}=13$  mm.) had been calibrated by Gay Lussac's method, the boiling point error determined, and the readings reduced to the hydrogen scale, the other was compared with it within the temperature interval; the last ( $1^{\circ}=15$  mm.) had also been calibrated by the same method, its freezing point error determined, and the readings also reduced to the hydrogen scale.

The water-bath, used for the purpose of heating, consisted of a tin vessel containing water, the temperature of which was controlled by a Reichert's regulator; inside this vessel was placed a calorimeter made of copper and tin, and consisting of three chambers filled with water, in the innermost of which the decomposition flask was placed, the surrounding water being stirred by a stream of fine bubbles of carbon dioxide from a Kipp's apparatus. The whole was closed with a lid furnished with suitable apertures.

In a control experiment, the temperature in the decomposition

flask, when filled with water only, was found to remain constant within  $\pm 0.1^\circ$  for several hours, but in actual working there was a gradual rise of about  $0.2^\circ$  at the earlier stage, due to the heat evolved by the decomposition of ammonium nitrite. The value of this, according to the determination of Thomson (*Prakt. Chem.*, 1880, [ii], 21, 449) is 71770 cal. per molecular proportion of salt, but according to Berthelot it equals 80400 cal. In certain experiments, a rise, in others a fall, of temperature was produced by the addition of certain reagents; these, when observed, were compensated as speedily as possible.

The whole apparatus, with the distillation flask empty, was heated up *slowly* until the required temperature was reached; then the ammonium nitrite solution, which had been heated up *quickly* to nearly the same temperature in another flask, was introduced, the rubber plug with the thermometer pressed in, and when the temperature had become constant, observations were commenced, the gas evolved in the meanwhile being collected and measured.

### *The Course of the Reaction.*

The decomposition of the ammonium nitrite starts slowly at first, as observed many years ago by Harcourt,\* owing to the retention of the nitrogen gas, then quickly reaches a maximum; from this point, it decreases in accordance with the law of mass action for a unimolecular reaction.

If  $V$  be the volume in c.c. of nitrogen evolved in time  $T$ , then

$$\log V/T(n) = \log V/T - n \log \text{const.} \quad (1),$$

for which  $n$  is the number of observations from the commencement.

The above equation can be transformed into the usual form:

$$\log A/A - = aT \quad (2).$$

The values in Series I, p. 740, were obtained in a set of observations made at a temperature of  $65^\circ$ ;  $\log \text{const.} = 0.0080$ .

The differences between the observed and calculated values, which rarely exceed 2 per cent., are mainly due to slight variations of temperature, since a rise or fall produces two errors in the same direction, firstly, an increase or decrease in the velocity of decomposition, and secondly, an expansion or contraction in the solution which causes more or less gas to be expelled.

The values in Series II, p. 740, were obtained in another series of

\* Blanchard (*loc. cit.*, *supra*) records a similar observation, apparently without being aware that it had been noted previously.



## SERIES I.

| No. of observation. | Value $V/T$ found. | Value $V/T$ calc. | No. of observation. | Value $V/T$ found. | Value $V/T$ calc. |
|---------------------|--------------------|-------------------|---------------------|--------------------|-------------------|
| —                   | 1.369              | —                 | 9                   | 1.134              | 1.155             |
| 1                   | 1.353              | 1.344             | 10                  | 1.118              | 1.138             |
| 2                   | 1.345              | 1.319             | 11                  | 1.087              | 1.118             |
| 3                   | 1.311              | 1.295             | 12                  | 1.068              | 1.097             |
| 4                   | 1.273              | 1.271             | 13                  | 1.079              | 1.078             |
| 5                   | 1.251              | 1.249             | 14                  | 1.030              | 1.057             |
| 6                   | 1.196              | 1.226             | 15                  | 1.040              | 1.038             |
| 7                   | 1.203              | 1.202             | 16                  | 1.009              | 1.020             |
| 8                   | 1.184              | 1.182             | 17                  | 0.940              | 1.001             |

observations in which benzoic sulphinide ("saccharin") had been added, which produced a considerable acceleration:

## SERIES II.

Temperature =  $61.8^{\circ}$ .  $\log \text{const.} = 0.0248$ .

| No. of observation. | Value $V/T$ found. | Value $V/T$ calc. | No. of observation. | Value $V/T$ found. | Value $V/T$ calc. |
|---------------------|--------------------|-------------------|---------------------|--------------------|-------------------|
| —                   | 5.986              | —                 | 11                  | 3.350              | 3.326             |
| 1                   | 5.885              | 5.825             | 12                  | 3.050              | 3.141             |
| 2                   | 5.561              | 5.561             | 13                  | 2.870              | 2.947             |
| 3                   | 5.274              | 5.252             | 14                  | 2.833              | 2.803             |
| 4                   | 5.083              | 4.961             | 15                  | 2.675              | 2.647             |
| 5                   | 4.857              | 4.698             | 16                  | 2.467              | 2.500             |
| 6                   | 4.525              | 4.441             | 17                  | 2.293              | 2.361             |
| 7                   | 4.260              | 4.180             | 18                  | 2.134              | 2.230             |
| 8                   | 4.018              | 3.948             | 19                  | 1.944              | 1.989             |
| 9                   | 3.840              | 3.729             | 20                  | 1.843              | 1.847             |
| 10                  | 3.589              | 3.522             | 21                  | 1.728              | 1.758             |

In the above series, the errors are of about the same order as in the preceding, so that whether the decomposition proceeds on its normal course or is accelerated, the same equation holds good.

• *Effect of Ammonia and its Derivatives.*

Arndt (*loc. cit. supra*) in the course of his investigations confirmed the older observation of Millon that the addition of free ammonia prevents, or hinders, according to the quantity added, the evolution of nitrogen from an aqueous solution of ammonium nitrite, and that even the addition of 1/800th part of ammonia reduces the rate by nearly two-thirds.

Some years ago (Trans., 1883, 43, 370), in the course of experiments on the rate of decomposition of ammonium nitrate, it was observed that a fragment of litharge added to a considerable mass of fused salt (about 100 grams) completely stopped the evolution of nitrous oxide, and the same result was obtained when ammonia gas was bubbled into the fused salt. The former experiment serves as a good lecture demonstration.

In order to ascertain whether ammonia liberated by the addition of a basic oxide would in like manner prevent the evolution of nitrogen from ammonium nitrite, an experiment was conducted as follows: a solution of the salt containing 2.24 grams in 70 c.c. (0.5 molecular) was heated for the purpose of determining the rate of decomposition, then 0.028 gram of lime was dropped in, which would liberate 0.017 gram of ammonia, and additional observations were recorded:

### SERIES III.

Temperature 70.7—70.9°.

| Before addition of lime. |               | After addition of lime. |               |
|--------------------------|---------------|-------------------------|---------------|
| No. of observation.      | Value $V/T$ . | No. of observation.     | Value $V/T$ . |
| 1                        | 1.572         | 8                       | 0.0639        |
| 2                        | 1.493         | 9                       | 0.0281        |
| 3                        | 1.477         | Reaction stopped        |               |
| 4                        | 1.398         |                         |               |
| 5                        | 1.343         |                         |               |
| 6                        | 1.274         |                         |               |
| 7                        | 1.186         |                         |               |

The ammonium nitrite originally present amounted to 2.2400 grams and 0.1468 gram was decomposed in the first part of the experiment, hence 2.0932 grams were present when the lime was added. This amount corresponds with 0.5569 gram of ammonia, of which only 0.0170 gram, or 3.06 per cent., was liberated by the lime.

It is thus evident that 3 per cent. of liberated ammonia, which remained dissolved in the solution at first impeded and then practically stopped the evolution of nitrogen, for even in the last observation nearly 36 minutes were required for the evolution of 1 c.c. of nitrogen.

A similar result was obtained with litharge, namely, the liberation of 1/9th of the total combined ammonia, this amount, which is equivalent to 1/350th of the total mass of ammonium nitrite, reduced the rate of evolution to 33 per cent. of its original value at the mean temperature 58.9°. Arndt found that 1/800th part of free ammonia

reduced the value to the same extent, but did not give temperature or other conditions of experiment.

In studying the effect produced by derivatives of ammonia, the liquids or solutions of solids were in all cases added by raising the rubber plug of the decomposition flask, dropping in a definite fraction of 1 c.c. by means of a 1 c.c. pipette graduated in 1/100ths, stirring with the thermometer, and then replacing the plug. As this operation only required a few seconds, the alteration of temperature was insignificant, and the time selected was that at which the rate of evolution of nitrogen had just passed its maximum value, the mean being taken of the observations before, during, and immediately after this point.

### Amines.

1. *Trimethylamine*, 33 per cent. solution, sp. gr. 12/12 = 0.9434. Ammonium nitrite present on adding the base = 2.0573 grams; weight of trimethylamine added = 0.036 gram. Mean temperature = 66.5°. Mean value of  $V/T$  before addition of trimethylamine = 1.561, after addition = 0.129. Thus the addition of 1.56 per cent. of trimethylamine reduces the rate of evolution of nitrogen to 8.2 per cent.

2. *Ethylamine*, 33 per cent. solution.—Ammonium nitrite present, on adding the base = 2.3493 grams; weight of base added = 0.0303 gram. Mean temperature = 59.5°.

Mean value of  $V/T$  before addition = 0.859; observations after addition = (i) 0.154, (ii) 0.046, and then evolution of gas practically came to an end.

3. *Amylamine*, 28 per cent. solution.—Ammonium nitrite present on adding the base = 2.1936 grams; weight of base added = 0.028 gram. Mean temperature = 63.6°.

| Mean value of $V/T$<br>before addition. | Values of $V/T$ after addition. |       |     |       |
|---|---------------------------------|-------|-----|-------|
|   | No.                             |       | No. |       |
| 1.274                                   | 1                               | 0.486 | 4   | 0.158 |
|   | 2                               | 0.235 | 5   | 0.129 |
|   | 3                               | 0.267 |     |       |

In this case, a more gradual reduction of the velocity was observed, the final rate being 10 per cent. of the original value.

4. *Aniline* (recently redistilled).—Ammonium nitrite present on adding the base = 1.6928 grams; weight of base added = 0.052 gram. Mean temperature = 64.5°. Mean value of  $V/T$  before addition



= 1.008, observations after addition = (i) 0.348, (ii) 0.14, (iii) 0.083. Thus the addition of 3 per cent. of aniline reduces the value to 8/100ths; at the conclusion of the experiment, the base, originally suspended in the liquid, had completely dissolved.

5. *Benzylamine*.—Ammonium nitrite present on adding the base = 2.3402 grams; weight of base added = 0.0987 gram. Mean temperature = 64.9°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.591                                   | 1                              | 0.314 | 3   | 0.061 |
|   | 2                              | 0.090 | 4   | 0.048 |

Thus, the addition of 4.2 per cent. benzylamine reduced the rate to 3/100ths of its former value, and then the rate became too slow for observation.

6.  *$\alpha$ -Picoline* (recently redistilled).—Ammonium nitrite present on adding the base = 2.0294 grams; weight of base added = 0.0952 gram. Mean temperature = 64.4°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.319                                   | 1                              | 0.811 | 4   | 0.235 |
|   | 2                              | 0.378 | 5   | 0.234 |
|   | 3                              | 0.240 |     |       |

Thus the addition of 4.7 per cent. of picoline reduced the rate to 18/100ths of its former value, at which point it remained nearly constant.

The foregoing results show that paraffinoid, benzenoid, and pyridine bases either reduce the rate of, or completely stop the decomposition of ammonium nitrite in aqueous solution.

### *Hydrazines.*

1. *Phenyldiazine*.—Ammonium nitrite present on adding the base = 2.1524 grams; weight of base added = 0.1099 gram. Mean temperature = 65.1°. Mean value of  $V/T$  before addition = 1.266; the evolution of gas stopped almost at once.

2. *Diphenylhydrazine* or *Hydrazobenzene*.—Ammonium nitrite present on adding the base = 2.1849 grams; 0.5 c.c. of a saturated solution of base added. Mean temperature = 64.5°.

| Mean value of $V/T$<br>before addition. | Values of $V/T$ after addition. |       |     |       |
|---|---------------------------------|-------|-----|-------|
|   | No.                             |       | No. |       |
| 1.210                                   | 1                               | 0.518 | 6   | 0.428 |
|   | 2                               | 0.459 | 7   | 0.429 |
|   | 3                               | 0.431 | 8   | 0.434 |
|   | 4                               | 0.419 | 9   | 0.432 |
|   | 5                               | 0.419 |     |       |

In this case, a reduction to 346/1000ths was observed, but at that point the rate remained constant during a considerable period.

#### *Oximes.*

1. *Acetaldoxime*.—Ammonium nitrite present on adding the acetaldoxime = 2.2766 grams; acetaldoxime added = 0.2892 gram. Mean temperature = 65.2°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.689                                   | 1                              | 1.183 | 4   | 0.260 |
|   | 2                              | 0.815 | 5   | 0.209 |
|   | 3                              | 0.429 |     |       |

2. *α-Benzaldoxime*.—Ammonium nitrite present on adding the benzaldoxime = 2.0487 grams; benzaldoxime added = 0.1844 gram. Mean temperature = 64.1°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.161                                   | 1                              | 1.214 | 6   | 0.625 |
|   | 2                              | 1.070 | 7   | 0.510 |
|   | 3                              | 0.976 | 8   | 0.445 |
|   | 4                              | 0.843 | 9   | 0.332 |
|   | 5                              | 0.765 | 10  | 0.242 |

3.  *$\beta$ -Benzaldoxime*.—Ammonium nitrite present on adding the benzaldoxime = 1.8849 gram; benzaldoxime added = 0.188 gram. Mean temperature = 64.7°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.082                                   | 1                              | 1.038 | 6   | 0.418 |
|   | 2                              | 0.913 | 7   | 0.367 |
|   | 3                              | 0.817 | 8   | 0.224 |
|   | 4                              | 0.689 | 9   | 0.182 |
|   | 5                              | 0.523 |     |       |

4. *Acetoxime*.—Ammonium nitrite present on adding the acetoxime = 1.8791 gram; acetoxime added = 0.113 gram. Mean temperature = 63°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 0.843                                   | 1                              | 0.764 | 4   | 0.312 |
|   | 2                              | 0.672 | 5   | 0.193 |
|   | 3                              | 0.505 |     |       |

The action of the above oximes is in all cases generally the same, being neither so effective nor so complete as in the case of the amines and hydrazines. The reduction apparently does not proceed in accordance with any simple equation, and it is probable that the reaction is also complicated.

#### *Amides.*

1. *Acetamide*, recrystallised four times previous to use. Ammonium nitrite present on adding acetamide = 1.8068 grams; weight of acetamide added = 0.1 gram. Mean temperature = 64.2°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.190                                   | 1                              | 1.375 | 5   | 1.383 |
|   | 2                              | 1.378 | 6   | 1.350 |
|   | 3                              | 1.240 | 7   | 1.327 |
|   | 4                              | 1.376 | 8   | 1.191 |



The addition of 5.5 per cent. of acetamide thus causes a temporary increase in the reaction, and the rate remains constant for some period of time, probably as the result of two opposing causes; on the one hand, the accelerating effect of the amide, and on the other, the diminution of mass. A repetition of the experiment with a larger quantity of acetamide gave a precisely similar result.

2. *Butyramide* (recently recrystallised). Ammonium nitrite present on adding the butyramide = 2.012 grams; weight of butyramide added = 0.1 gram. Mean temperature = 63.8°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |       |     |       |
|---|--------------------------------|-------|-----|-------|
|   | No.                            |       | No. |       |
| 1.386                                   | 1                              | 1.493 | 4   | 1.345 |
|   | 2                              | 1.389 | 5   | 1.248 |
|   | 3                              | 1.325 | 6   | 1.211 |

3. *Benzamide* dissolved in alcohol so as to form a saturated solution, of which 0.5 c.c. was added. Mean temperature = 65.9°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |        |                                |
|---|--------------------------------|--------|--------------------------------|
|   | No.                            | Found. | Calc. log. const. =<br>0.0140. |
| 1.702                                   | 1                              | 1.575  | —                              |
|   | 2                              | 1.539  | 1.522                          |
|   | 3                              | 1.507  | 1.474                          |
|   | 4                              | 1.423  | 1.427                          |
|   | 5                              | 1.375  | 1.381                          |
|   | 6                              | 1.308  | 1.338                          |
|   | 7                              | 1.293  | 1.295                          |
|   | 8                              | 1.209  | 1.268                          |

From these results it appears that benzamide neither accelerates nor retards the reaction, as the rate of decomposition after its addition is in accordance with the equation given above.

4. *Urea*. Ammonium nitrite present on adding urea = 1.8944 grams; weight of urea added = 0.1 gram. Mean temperature = 63.1°.

| Mean value of $V/T$<br>before addition. | Value of $V/T$ after addition. |        |                               |
|---|--------------------------------|--------|-------------------------------|
|   | No.                            | Found. | Calc. log. const. =<br>0.022. |
| 0.840                                   | 1                              | 0.803  | —                             |
|   | 2                              | 0.768  | 0.768                         |
|   | 3                              | 0.704  | 0.730                         |
|   | 4                              | 0.693  | 0.694                         |
|   | 5                              | 0.658  | 0.660                         |
|   | 6                              | 0.641  | 0.637                         |
|   | 7                              | 0.602  | 0.597                         |

Urea, like benzamide, neither accelerates nor retards the reaction.

### *Imides.*

Of the imides sufficiently soluble in water to be applicable for this investigation, only one, namely, benzoic sulphinide or "saccharin," was tried, and a saturated aqueous solution was made.

Ammonium nitrite present on adding "saccharin" = 2.2237 grams ; "saccharin" added = 0.125 gram. Mean temperature = 61.8°.

Value of  $V/T$  before addition = 1.050 ; immediately after addition, = 5.060, subsequently rising after three observations to 5.946 and then to 5.986, from which point the rate decreased uniformly, the remaining observations being given in Series II (*vide supra*). It appears, therefore, that the addition of this imide immediately increases the rate of evolution of nitrogen by 5—6 times its value before addition, and although the reaction proceeds according to the law of mass, yet even after a large part of the ammonium nitrite had been decomposed, the accelerating effect still continued.

The results detailed above may be summarised as follows : amines, hydrazines, and oximes retard or completely stop the decomposition of ammonium nitrite ; amides produce either a slight or temporary acceleration ; whilst imides produce a considerable acceleration, without, however, altering the law to which the reaction can be referred. It is not proposed to offer any explanation of these several phenomena ; the first and third come within the general category of catalysis, but neither a name nor a classification can be considered to be an explanation.

### *The Formation of Ammonia or Acid.*

Arndt, who prepared the ammonium nitrite in solution by the decomposition of barium nitrite with ammonium sulphate, observed

that such solutions became alkaline after a certain time, a result which he attributed to the formation of ammonia. He writes: "Bei einigen Stundenlang dauernden Messingsreihen was es mir aufgefallen dass in der Ammoniumnitritlösung Spuren von Ammoniak frei geworden waren, die der Lösung alkalische Reaction verstehen."

It is somewhat difficult to understand this observation, having regard to the statement by the same writer that even such a small quantity as 1/800th part of free ammonia reduces the rate to nearly one-third (compare *supra*); further, most solutions of ammonium salts become acid when heated.

In order to examine this point, ammonium nitrite solutions (prepared from silver nitrite), which generally contained a trace of free acid, were titrated with a very dilute solution of ammonia, then heated for different periods of time and again titrated. The amount of salt present before and after the experiment was estimated by potassium permanganate, and hence the percentage decomposition ascertained. The results are given in the following table:

| Acids in parts per 10,000. |        | Percentage decomposition. |
|----------------------------|--------|---------------------------|
| Before.                    | After. |                           |
| 6.6                        | 6.6    | 4.9                       |
| 0.3                        | 0.3    | 10.31                     |
| 1.3                        | 1.0    | 13.53                     |
| 0.2                        | 0.2    | 59.63                     |
| trace                      | trace  | 66.88                     |

From the above results, there does not appear to be any indication of the formation of ammonia, and in the last two observations the reaction was continued for several hours.

*Presence of Barium Sulphate and Finely-divided Particles.*

As mentioned above, Arndt prepared the ammonium nitrite solutions from barium nitrite and ammonium sulphate *in situ*, and he stated that the presence of the finely-divided, precipitated barium sulphate made no difference in the rate of evolution of nitrogen. In my previous experiments (*loc. cit.*), I observed that the addition of silica and pumice to a solution when heated and evolving gas, caused a temporary increase in the rate of evolution; precipitated barium sulphate, although not tried in this particular decomposition, was found to be an effective material in other cases.



As the observations of Arndt and myself appear to be discrepant, this point was examined incidentally. Finely-divided barium sulphate was prepared by treating, at the ordinary temperature, a solution of recrystallised barium chloride (1 litre = 0.1 BaCl<sub>2</sub>) with a solution of recrystallised copper sulphate having an equivalent concentration. The precipitate was washed by decantation only until free from impurities, other than a negligible trace of chloride; it was then ignited in a platinum crucible, rubbed up in an agate mortar, and finally sifted through fine muslin. In order to examine the degree of fineness, the particles were examined under a microscope with a magnification of 1000 diameters, and their average diameter found to be 1—2  $\mu$ . Without entering fully into the details of the experiments, it need only be stated that, on the one hand, the addition of this precipitate to a solution evolving gas caused a temporary increase in the rate of the evolution, the effect being quite transitory; on the other hand, in a comparative experiment in which two solutions, one without and the other with, barium sulphate were heated side by side, it was found that at first the evolution of gas was more rapid from the solution containing the precipitate, but subsequently the rates of evolution became equal. The barium sulphate, therefore, merely produces an alteration in the quantity of nitrogen gas stored within the solution.

The main points of the present communication may be summarised as follows:

(1) The decomposition of ammonium nitrite into nitrogen and water proceeds according to the general law

$$\log A/A - x = aT,$$

whether in the presence or absence of an accelerator.

(2) This decomposition is either impeded or stopped by ammonia liberated in the solution by the addition of metallic oxides; it is also similarly affected by amines and hydrazines, and to a less degree by oximes.

(3) The decomposition is temporarily accelerated by amides of the paraffin series, but other amides are ineffective.

(4) Benzoic sulphinide, the only imide tried, produced a considerable acceleration.

(5) Solutions of ammonium nitrite, prepared from silver nitrite and ammonium chloride, do not become alkaline in the course of decomposition.

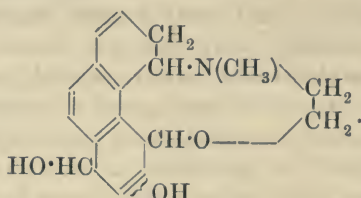
I have to express my obligations to Mr. H. C. Buck for assistance in the course of this investigation.

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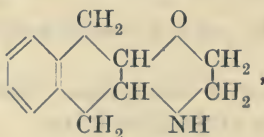
LXXVII.—*The Electrolytic Reduction of Pheno- and Naphtho-morpholones.*

By FREDERIC HERBERT LEES and FRANK SHEDDEN.

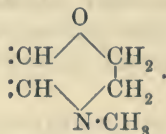
It has been shown by Knorr and others that morphine is an *N*-methyl-dihydroxytetrahydrophenanthromorpholine, having, with a high degree of probability, the constitution:



From the observation of Leubuscher (compare Knorr, *Annalen*, 1899, 307, 172, and *Ber.*, 1899, 32, 742—749) that *N*-alkyl derivatives of the synthetical base tetrahydronaphthomorpholine (naphthalan-morpholine), represented by the formula:



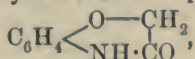
have a physiological action closely resembling that of morphine, it would appear that this alkaloid owes its narcotic action to the presence of the residue:



The two carbon atoms which are common to the morpholine residue and the partially reduced aromatic nucleus are, in the case of the synthetical base, contiguous, whereas, in that of morphine they occupy a *peri*-position; this difference, however, does not affect the physiological action. In view of the foregoing relationship, it appeared of interest to consider the production of some morpholine derivatives by such methods as would render them available for therapeutic use, in case a systematic study of their physiological action should prove favourable. Some experiments with this object in view were initiated by one of us in association with S. B. Schryver, but were

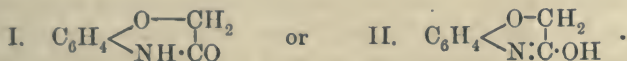
for a time discontinued. By agreement with Dr. Schryver, the work has been resumed by the authors, who now present some of their results.

Since Tafel (*Ber.*, 1899, 32, 68, and 1900, 33, 2209) had obtained such excellent results by the electrolytic reduction of numerous simple and complex amides, whereby the groupings  $-\text{CO}\cdot\text{NH}_2$  and  $-\text{CO}\cdot\text{NH}\cdot\text{R}$  were respectively converted into those of the types  $-\text{CH}_2\cdot\text{NH}_2$  and  $-\text{CH}_2\cdot\text{NH}\cdot\text{R}$ , it was thought that the application of the same method to such cyclic amides as phenomorpholone,



and its analogues and homologues might lead to the production of the corresponding morpholines. In certain cases, these derivatives were obtained, but the yields were small owing to the remarkable and unexpected instability of the morpholone ring under the reducing conditions employed.

From its mode of formation by the reduction of *o*-nitrophenoxy-acetic acid, phenomorpholone may be regarded as either the lactam or lactim of the *o*-amino-acid :



Wheeler and Barnes (*Amer. Chem. J.*, 1898, 20, 555), as the result of an extended study of its *O*- and *N*-ethers, prepared from the silver and sodium derivatives respectively, have decided on formula I for phenomorpholone. The more recent investigations of Titherley (*Trans.*, 1901, 79, 409), Hantzsch (*Ber.*, 1902, 35, 2717), and Lander (this vol., 414), however, support the view that certain compounds containing metallic radicles display, when in solution, the phenomenon of tautomerism, and this might also apply to the corresponding hydrogen compounds. These considerations render it very difficult to decide which of the complexes  $-\text{NH}\cdot\text{CO}-$  and  $-\text{N}:\text{C}(\text{OH})-$  is present in the molecules of the hydrogen compounds.

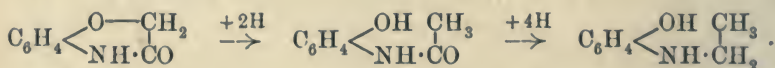
A fact which has supported the supposition that the anilides actually contain the grouping  $-\text{CO}\cdot\text{NH}-$  is that the boiling point of *O*-ethylformanilide is  $82^\circ$  lower than that of formanilide, whereas the *O*-ethyl ethers of true oxymethylene compounds boil at higher temperatures than the parent substances (Claisen, *Annalen*, 1895, 287, 362). A comparison of the boiling points of other substituted amides and of phenomorpholone with those of their respective *O*- and *N*-methyl and ethyl ethers also confirms the above supposition (compare Lander, *Trans.*, 1901, 79, 691), and at the same time shows that phenomorpholone falls within the same category.



|   | N-Ethers.             | O-Ethers.            | Hydrogen compounds. |
|---|-----------------------|----------------------|---------------------|
| Methyl acetanilide .....                | 253°                  | 197°                 | 304°                |
| Ethyl acetanilide .....                 | 258                   | 207                  |                     |
| Methyl aceto- <i>o</i> -toluidide ..... | 252                   | 212                  | 296                 |
| Ethyl aceto- <i>o</i> -toluidide .....  | 255                   | 222                  |                     |
| Ethyl aceto- <i>p</i> -toluidide .....  | 258                   | 232                  | 307                 |
| Methyl phenomorpholone.....             | 290 (156°,<br>14 mm.) | 135—136°<br>(21 mm.) | 325                 |
| Ethyl phenomorpholone .....             | 287 (158°,<br>15 mm.) | 135—136°<br>(16 mm.) |                     |

These physical data favour the conclusion of Wheeler and Barnes (*loc. cit.*), and such evidence will probably be found to be of more value than that of a purely chemical nature in clearing up the anomalies due to tautomerism, which exist among substances of the amide class and their derivatives.

When phenomorpholone, dissolved in 90 per cent. sulphuric acid, was electrolytically reduced according to Tafel's method (*Ber.*, 1900, 33, 2209), and the temperature of the cell kept below 30°, no phenomorpholine was found, but acetyl-*o*-aminophenol, ethyl-*o*-aminophenol and isoacetyl-*o*-aminophenol were isolated as the products of the reduction. The only explanation of the formation of these substances is that the morpholone ring is ruptured on reduction, according to the scheme:



As far as we are aware, such a disruption of an aryloxy-derivative by reduction at a low temperature has not hitherto been noticed.

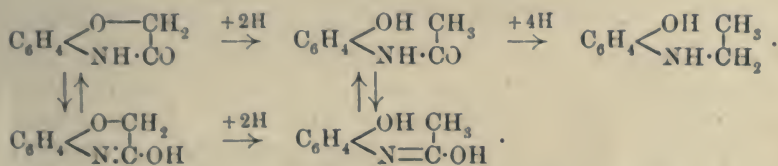
The isoacetyl-*o*-aminophenol melted at 190° with decomposition, was soluble in dilute potassium hydroxide, and its alcoholic solution gave a bluish-green coloration with ferric chloride. When heated at its melting point, it evolved a molecular proportion of water, forming an oil which distilled completely at 190°, and proved to be ethenyl-*o*-aminophenol,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C} \cdot \text{CH}_3$ .

This behaviour distinguished it from acetyl-*o*-aminophenol, which melts at 204° and is only partially converted into the ethenyl base by distillation, this taking place at a temperature considerably higher than its melting point.

The comparative ease with which isoacetyl-*o*-aminophenol parts with water, forming ethenyl-*o*-aminophenol, leads us to suggest that it has the structure  $\text{C}_6\text{H}_4 \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{N} : \text{C}(\text{OH}) \cdot \text{CH}_3 \end{array}$ , which represents it as the

enolic modification of acetyl-*o*-aminophenol. Its formation might be explained by assuming that phenomorpholone exists in solution as a mixture of its tautomeric isomerides, which respectively suffer disruption during reduction in the manner already shown, giving rise to the two corresponding isomeric acetyl aminophenols. Then, assuming that the rate of formation of the imino-form of acetyl-*o*-aminophenol exceeds that of its transformation into the amino-modification, it is only necessary that the contents of the electrolytic cell should be diluted at an appropriate stage in order to cause the separation of the less basic isomeride.

According to the formula suggested, isoacetyl-*o*-aminophenol is the hydroxy derivative of an *N*-arylacetiminoether, and is the first example of this class of compound. The following scheme possibly represents the reduction of phenomorpholone :



On electrolytic reduction, *N*-methylphenomorpholone also, for the most part, underwent disruption in the same way, and gave as the principal products *N*-acetylmethyl-*o*-aminophenol and *N*-methylethyl-*o*-aminophenol. In this case, however, a yield of about 10 per cent. of *N*-methylphenomorpholine was obtained, this product being identical in all respects with that prepared by Knorr by another method (*Ber.*, 1889, 22, 2081, and 1899, 32, 732).

Attempts to prepare a morpholone from  $\alpha$ -naphthol according to the method which so readily gives phenomorpholone were without success, owing to the very sparing solubility in water of the sodium and potassium derivatives of  $\beta$ -nitro- $\alpha$ -naphthol, which renders their interaction with sodium chloroacetate impracticable, the latter becoming almost entirely hydrolysed before the desired condensation has proceeded even to a small extent. An attempt to prepare the necessary  $\beta$ -nitro- $\alpha$ -naphthoxyacetic acid by another method, namely, by nitrating  $\alpha$ -naphthoxyacetic acid, was also unsuccessful, as the resulting nitro-acid did not yield a morpholone on reduction, and was probably the  $\alpha'$ -nitro-acid, the nitration having taken place as in the case of  $\alpha$ -naphthyl ethyl ether (compare Heermann, *J. pr. Chem*, 1891, 44, 240).

On the other hand,  $\alpha$ -nitro- $\beta$ -naphthoxyacetic acid was easily obtained either by nitrating  $\beta$ -naphthoxyacetic acid, or by condensing the sodium salt of  $\alpha$ -nitro- $\beta$  naphthol with sodium chloroacetate. On





current of 6 amperes for 3 hours, with the temperature at  $35^{\circ}$ , the contents of the cell were poured into water (500 c.c.), and the precipitate, which for the most part consisted of lead sulphate, collected, washed until free from acid, and dried.

*isoAcetyl-o-aminophenol*,  $C_6H_4(OH)N:C(CH_3)\cdot OH$ .

By extracting the above precipitate with hot alcohol, filtering and concentrating, the *isoacetyl-o-aminophenol* separated in colourless, lustrous leaflets, which, after several recrystallisations from the same solvent, melted at  $190$ — $191^{\circ}$  with evolution of water vapour :

0.1164 gave 0.27  $CO_2$  and 0.0644  $H_2O$ .  $C = 63.3$  ;  $H = 6.1$ .

$C_8H_9O_2N$  requires  $C = 63.6$  ;  $H = 6.0$  per cent.

This product is somewhat more acidic than *acetyl-o-aminophenol*, a fact which was shown by its separation when the strongly acid contents of the electrolytic cell were diluted with water, whilst, on the other hand, the *acetyl-o-aminophenol*, which was present in larger amount, remained dissolved. The former is soluble in dilute aqueous solutions of the caustic alkalis, and its alcoholic solution develops a bluish-green coloration with ferric chloride.

The amounts of this substance obtained from a number of reductions varied considerably ; in one case, 3.5 grams resulted, in others, not more than 0.5 gram was obtained, and in many experiments this product could not be isolated.

When *isoacetyl-o-aminophenol* (3 grams) was gently heated in a small distillation apparatus until it melted, a vigorous evolution of steam took place. The residual oil distilled completely at  $180$ — $195^{\circ}$  ; this product was then dissolved in ether, dried with potassium carbonate and redistilled, when it boiled at  $205$ — $207^{\circ}$  :

0.1756 gave 0.4641  $CO_2$  and 0.0869  $H_2O$ .  $C = 72.1$  ;  $H = 5.5$ .

$C_8H_7ON$  requires  $C = 72.2$  ;  $H = 5.3$  per cent.

The substance was a base, had a characteristic odour, and when its solution in dilute hydrochloric acid was boiled for a few minutes, cooled, and then sown with a trace of *acetyl-o-aminophenol*, a quantity of this substance separated, which melted at  $205^{\circ}$ . The base was thus shown to be identical with *ethenyl-o-aminophenol*,  $C_6H_4\begin{smallmatrix} \diagup O \\ N \diagdown \end{smallmatrix}C\cdot CH_3$  (Ladenburg, *Ber.*, 1876, 9, 1524).

*Acetyl-o-aminophenol*.—The acid filtrate from the precipitate of lead sulphate and *isoacetyl-o-aminophenol* was nearly neutralised with calcium carbonate, filtered from calcium sulphate, and while still acid, extracted several times with ether. The ethereal solution yielded a crystalline product, which, after recrystallisation, melted at  $205^{\circ}$  and

had all the properties of acetyl-*o*-aminophenol, being definitely identified as such by the fact that when heated at 140° for 3 hours with concentrated hydrochloric acid, it was decomposed into acetic acid and *o*-aminophenol (m. p. 175—176°).

*Ethyl-o-aminophenol*.—The residual aqueous liquid from the ethereal extract was made alkaline with sodium carbonate, and again extracted repeatedly with ether. The ethereal solution was washed with a little water and then shaken up with dilute hydrochloric acid. From this acid extract, after evaporation in a vacuum desiccator, a quantity of pink crystals was obtained. These were purified by recrystallising from a mixture of alcohol and acetone, and then melted at 220°:

0.1156 gave 0.2336 CO<sub>2</sub> and 0.0722 H<sub>2</sub>O. C = 55.1; H = 6.9.

0.2202 „ 0.1798 AgCl. Cl = 20.2.

C<sub>8</sub>H<sub>11</sub>ON, HCl requires C = 55.3; H = 6.9; Cl = 20.5 per cent.

That this was the hydrochloride of ethyl-*o*-aminophenol was shown by the fact that on decomposition with dilute sodium carbonate it gave the crystalline base melting at 112°, from which the nitroso-derivative, decomposing at 121°, was easily obtained.

#### *Electrolytic Reduction of N-Methylphenomorpholone.*

*N*-Methylphenomorpholone (20 grams) was dissolved in 60 per cent. sulphuric acid (100 c.c.), and electrolytically reduced in the inner cell. The outer cell contained 40 per cent. acid. A current of 12 amperes was passed for 3 hours, the temperature being maintained below 35° by a continuous stream of cold water flowing through the hollow leaden cathode. The contents of the cell were then diluted with water (500 c.c.), and the solution filtered to remove lead sulphate.

*N*-Acetylmethyl-*o*-aminophenol, C<sub>9</sub>H<sub>9</sub>(OH)·N(CH<sub>3</sub>)·CO·CH<sub>3</sub>.

The acid filtrate from the lead sulphate was extracted repeatedly with ether. The ethereal solution yielded on evaporation a white, crystalline cake, which, when recrystallised from methylal, separated in glistening needles melting at 150°:

0.1055 gave 0.2542 CO<sub>2</sub> and 0.0649 H<sub>2</sub>O. C = 65.7; H = 6.8.

C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>N requires C = 65.5; H = 6.7 per cent.

The substance was shown to be *N*-acetylmethyl-*o*-aminophenol by heating it at 140° for 3 hours with concentrated hydrochloric acid, when it was decomposed into acetic acid and *N*-methyl-*o*-aminophenol; the latter, when crystallised from a mixture of benzene

and light petroleum, formed colourless, rhombic leaflets melting at 96—97°: \*

0.0995 gave 0.2493 CO<sub>2</sub> and 0.066 H<sub>2</sub>O. C = 68.3; H = 7.4.

C<sub>7</sub>H<sub>9</sub>ON requires C = 68.3; H = 7.3 per cent.

*N*-Acetylmethyl-*o*-aminophenol is readily soluble in alcohol, and can be recrystallised from hot water; with ferric chloride, its aqueous solution develops a purple coloration, changing to brown.

In addition to the amount of *N*-acetylmethyl-*o*-aminophenol isolated by the above extraction with ether, a further quantity was obtained, after removing the bases, by neutralising the alkaline liquid with sulphuric acid, evaporating to dryness, and extracting the residue with hot alcohol.

*N*-Methylethyl-*o*-aminophenol, C<sub>6</sub>H<sub>4</sub>(OH)·N(CH<sub>3</sub>)·C<sub>2</sub>H<sub>5</sub>, and *N*-Methyl-phenomorpholine.

The acid liquid, from which some of the acetylmethyl-*o*-aminophenol had been removed, was made alkaline with sodium carbonate and extracted with ether; the ethereal extract was dried with potassium carbonate, concentrated to 70 c.c., and mixed with 20 c.c. of absolute alcohol. Hydrochloric acid gas was then passed into the purple solution until the colour changed to green. The glistening crystals, which separated on leaving the solution overnight, when recrystallised from a mixture of alcohol and ether, formed well-defined, colourless double-pyramids melting at 150°. The substance proved to be *N*-methylethyl-*o*-aminophenol hydrochloride:

0.1289 gave 0.2714 CO<sub>2</sub> and 0.0856 H<sub>2</sub>O. C = 57.4; H = 7.4.

C<sub>9</sub>H<sub>13</sub>ON, HCl requires C = 57.6; H = 7.5 per cent.

It is very freely soluble in water or alcohol. Its aqueous solution, on treatment with the reagents mentioned, behaved as follows:

|  |   |
|--|---|
| Ferric chloride .....                      | A brownish-purple coloration.                       |
| Hydrochloric acid and sodium nitrite ..... | A pale yellow coloration.                           |
| Chromic acid .....                         | A blood-red coloration.                             |
| Sodium carbonate .....                     | An oily base completely soluble in caustic alkalis. |

\* Seidel (*J. pr. Chem.*, 1890, 42, 453) gives the melting point of methyl-*o*-aminophenol as "above 80° with decomposition." He was obviously dealing with an impure specimen, for apart from the fact that his melting point is far too low, the percentage of carbon as calculated from his analytical figures is 61.1, although incorrectly given as 67.9.



*N*-Methylphenomorpholine hydrochloride was obtained from the ether-alcohol mother liquor from the foregoing hydrochloride, by shaking repeatedly with water, rendering the aqueous solution alkaline with sodium carbonate, and extracting with ether. After drying with potassium carbonate, the ethereal solution was concentrated considerably, a little absolute alcohol added, and hydrochloric acid passed in as before. In this way, a crystalline hydrochloride was obtained which melted at  $166^{\circ}$ , and on recrystallisation from alcohol, in which it was only sparingly soluble in the cold, formed long, glistening needles, which then melted at  $167\text{--}168^{\circ}$  to an emerald-green oil.

0.1204 gave 0.2587  $\text{CO}_2$  and 0.0728  $\text{H}_2\text{O}$ .  $\text{C}=58.6$  ;  $\text{H}=6.7$ .

$\text{C}_9\text{H}_{11}\text{ON}, \text{HCl}$  requires  $\text{C}=58.2$  ;  $\text{H}=6.5$  per cent.

The melting point of *N*-methylphenomorpholine hydrochloride is given by Knorr (*Ber.*, 1889, 22, 2098) as  $162^{\circ}$ . The identity of this product with methylphenomorpholine was fully established as follows. The addition of caustic alkali to a solution of the hydrochloride precipitated an oily base of characteristic odour which was quite insoluble in excess of the reagent. The base was extracted and distilled, when it boiled entirely at  $252\text{--}254^{\circ}$  under a pressure of 769 mm, and was obtained as a colourless oil, which gave the characteristic oxidation colour reactions of methylphenomorpholine.

0.1017 gave 0.2693  $\text{CO}_2$  and 0.0682  $\text{H}_2\text{O}$ .  $\text{C}=72.2$  ;  $\text{H}=7.5$ .

$\text{C}_9\text{H}_{11}\text{ON}$  requires  $\text{C}=72.5$  ;  $\text{H}=7.4$  per cent.

The methiodide was also formed ; it melted at  $195\text{--}200^{\circ}$  with evolution of methyl iodide.

#### *Preparation of N-Methyl- $\beta$ -naphthomorpholine.*

*$\alpha$ -Nitro- $\beta$ -naphthoxyacetic acid*,  $\text{C}_{10}\text{H}_6(\text{NO}_2) \cdot \underset{\alpha}{\text{O}} \cdot \underset{\beta}{\text{CH}_2} \cdot \text{CO}_2\text{H}$ , can be obtained in two ways, but more conveniently by nitrating  $\beta$ -naphthoxyacetic acid. This acid was prepared from  $\beta$ -naphthol and chloroacetic acid under conditions which varied somewhat from those given by Spica (*Gazzetta*, 1886, 16, 441), in that the hot solution of the sodium salts, after the condensation, was not acidified, and subsequently treated with ammonium carbonate and ether to remove  $\beta$ -naphthol, but was allowed to cool, when the sodium salt of the required acid separated in an almost pure state, and in large quantity.

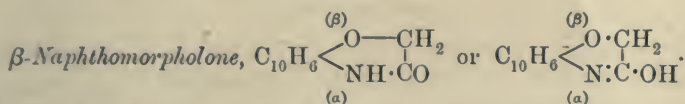
$\beta$ -Naphthoxyacetic acid (100 grams) was dissolved in glacial acetic acid (600 c.c.), the solution cooled, and 70 c.c. of nitric acid (sp. gr. 1.42) cautiously added with stirring. On allowing the mixture to remain for 2 hours, the nitro-acid separated, and, after washing with

acetic acid, melted at 185°. On recrystallisation from acetic acid, it separated in short, flattened, yellow prisms which melted at 188—189°. The yield amounted to 80 per cent. of the  $\beta$ -naphthoxyacetic acid employed :

0.1148 gave 0.2458 CO<sub>2</sub> and 0.0372 H<sub>2</sub>O. C = 58.4 ; H = 3.6.

C<sub>12</sub>H<sub>9</sub>O<sub>3</sub>N requires C = 58.3 ; H = 3.6 per cent.

In order to prove that the direct nitration of  $\beta$ -naphthoxyacetic acid led to the production of the  $\alpha$ -nitro-compound,  $\alpha$ -nitro- $\beta$ -naphthol (Stenhouse and Groves, *Annalen*, 1877, 189, 151), prepared from the  $\alpha$ -nitroso-compound (Groves, *Trans.*, 1884, 45, 295), was condensed with chloroacetic acid by boiling an aqueous solution of their respective potassium salts in molecular proportion, for several hours. The hot aqueous liquid was then decanted from some  $\alpha$ -nitro- $\beta$ -naphthol, which had separated owing to a side reaction, concentrated considerably, and, while still hot, acidified with concentrated hydrochloric acid. The nitro-acid then crystallised out, and after recrystallisation from acetic acid melted at 188—189°. It was in all respects identical with the acid prepared according to the foregoing method.



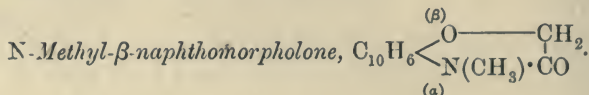
$\alpha$ -Nitro- $\beta$ -naphthoxyacetic acid (100 grams) was dissolved in hot glacial acetic acid (400 c.c.) and a quantity of boiling water (200 c.c.) added. This was followed by the cautious addition of iron filings (80 grams) to the hot solution. When the reaction became too vigorous, it was checked by placing the flask in water for a moment, the reduction being completed by heating on the water-bath for an hour. The mixture, after dilution with an equal volume of water, was cooled and filtered. The precipitate contained the  $\beta$ -naphthomorpholone, mixed with a considerable amount of iron acetate which was removed by suspending the precipitate in a 20 per cent. solution of caustic soda, adding hot alcohol (500 c.c.), boiling for a short time, and filtering. The filtrate, when concentrated by distillation, diluted with water, and acidified with hydrochloric acid, deposited the  $\beta$ -naphthomorpholone in a nearly pure state, the yield amounting to 80—90 per cent. of the theoretical. On recrystallisation from acetic acid, the compound formed fine, glistening needles which melted at 215—216° :

0.1142 gave 0.3026 CO<sub>2</sub> and 0.0472 H<sub>2</sub>O. C = 72.3 ; H = 4.6.

C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N requires C = 72.4 ; H = 4.5 per cent.

$\beta$ -Naphthomorpholone closely resembles its analogue, phenomorpho-

lone; it is acidic in character, being readily soluble in caustic alkalis, but not in alkali carbonates. Its acidic hydrogen atom is readily replaceable by metallic and alkyl radicles.



This was readily obtained and in theoretical amount by the interaction of the sodium derivative of  $\beta$ -naphthomorpholone with methyl iodide, in alcohol at  $100^\circ$ . The addition of water to the hot liquid precipitated the compound in white needles. When recrystallised from absolute alcohol, it formed long, colourless needles which melted at  $84\text{--}85^\circ$ :

0.1157 gave 0.3095  $\text{CO}_2$  and 0.0542  $\text{H}_2\text{O}$ . C = 73.0; H = 5.2.

$\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$  requires C = 73.2; H = 5.2 per cent.

It is quite insoluble in caustic alkalis, and not appreciably dissolved by acids, except when the latter are concentrated.

#### *Electrolytic Reduction of N-Methyl- $\beta$ -naphthomorpholone.*

The preceding substance (20 grams), dissolved in 80 per cent. sulphuric acid (100 c.c.), was electrolytically reduced in the inner cell. The outer cell contained 60 per cent. acid, and a current of 4.5 amperes was maintained for 4 hours, while the temperature was kept below  $22^\circ$  by passing water through the hollow cathode. The inner cell contents were then diluted with water (500 c.c.) and filtered from lead sulphate, together with a little methyl- $\beta$ -naphthomorpholone which had escaped reduction. The filtrate was made alkaline with sodium carbonate, and extracted repeatedly with ether. The ethereal solution was washed with water, and then extracted with hydrochloric acid to remove the bases; it was finally dried and the ether removed. The residue consisted entirely of a small amount of unchanged methyl- $\beta$ -naphthomorpholone.

The hydrochloric acid solution of the bases was made alkaline with sodium carbonate, and these compounds again taken up with ether. The ethereal solution was dried with potassium carbonate, and the ether removed. The residual basic oil obtained in this way from 200 grams of the morpholone amounted to 125 grams. It was fractionally distilled under a pressure of 40 mm., when the following fractions were obtained as pale yellow oils:

|   |                                    |              |
|---|------------------------------------|--------------|
| I. B. p. $195\text{--}198^\circ$ = 65 grams.  | III. B. p. $205\text{--}215^\circ$ | } = 25 grams |
| II. B. p. $193\text{--}205^\circ$ = 16 grams. | IV. „ $215\text{--}225^\circ$      |              |



Fractions I and II were for the most part soluble in cold 10 per cent. caustic potash, and the former soon became crystalline; fractions III and IV, on the other hand, remained oily, and were practically insoluble in caustic potash. These results indicated that the principal product was of phenolic character, and that a smaller amount of a morpholine had also been produced.

*N-Methylethyl- $\alpha$ -amino- $\beta$ -naphthol*,  $C_{10}H_6(OH) \cdot N(C_2H_5) \cdot CH_3$ .

After several unsuccessful attempts to prepare crystalline salts of *N-methylethyl- $\alpha$ -amino- $\beta$ -naphthol* and the mineral acids from fractions I and II, it was found that the *sulphocamphylate* answered the purpose. The combined fractions were therefore converted into this salt, which, when recrystallised from water, formed clusters of prismatic needles containing a molecule of water:

0.5512 of the air-dried salt at  $115^\circ$  lost 0.0208.  $H_2O = 3.8$ .

0.3796 " " gave, after fusion with  $Na_2CO_3$ , 0.1988  $BaSO_4$ .  $S = 7.2$ .

$C_{13}H_{15}ON, C_9H_{14}O_5S, H_2O$  requires  $H_2O = 4$  and  $S = 7.1$  per cent.

The salt is readily soluble in alcohol, but on adding ether it separates again in hard, glistening, anhydrous prisms melting at  $203-204^\circ$ . *N-Methylethyl- $\alpha$ -amino- $\beta$ -naphthol* was easily obtained from the pure *sulphocamphylate*. On distillation under 40 mm. pressure, it boiled completely at  $193^\circ$ , being obtained as a yellow oil, which, on cooling, set to a hard, crystalline mass of needles melting at  $25-27^\circ$ :

0.1034 gave 0.2942  $CO_2$  and 0.0712  $H_2O$ .  $C = 77.6$ ;  $H = 7.6$ .

$C_{13}H_{15}ON$  requires  $C = 77.6$ ;  $H = 7.5$  per cent.

*N-Methylethyl- $\alpha$ -amino- $\beta$ -naphthol*, although practically colourless when freshly distilled, soon darkens on exposure to the air; it is easily soluble in dilute solutions of the caustic alkalis, and its solution in absolute alcohol develops a deep-brown coloration with ferric chloride. The addition of sodium nitrite to its solution in dilute hydrochloric acid gives no coloration. The *hydriodide* was prepared in acetone solution and precipitated by ether in rosettes of fine needles, which melted at  $183^\circ$  with evolution of hydrogen iodide:

0.1698 gave 0.2978  $CO_2$  and 0.0789  $H_2O$ .  $C = 47.8$ ;  $H = 5.2$ .

$C_{13}H_{15}ON, HI$  requires  $C = 47.4$ ;  $H = 4.9$  per cent.

The *acetyl* derivative is a colourless, stable oil, which boils at  $212-215^\circ$  under 40 mm. pressure:

0.1142 gave 0.3107  $\text{CO}_2$  and 0.0736  $\text{H}_2\text{O}$ .  $\text{C} = 74.2$ ;  $\text{H} = 7.2$ .

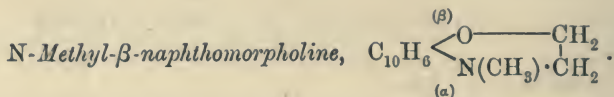
$\text{C}_{13}\text{H}_{14}(\text{C}_2\text{H}_3\text{O}_2)\text{N}$  requires  $\text{C} = 74.1$ ;  $\text{H} = 7.0$  per cent.

Its solution in absolute alcohol gives with ferric chloride a green coloration, a similar colour change being produced by adding sodium nitrite to a solution of the ester in dilute hydrochloric acid.

*Action of Oxidising Agents.*—When *N*-methylethyl- $\alpha$ -amino- $\beta$ -naphthol is shaken in the cold with aqueous solutions of mild oxidising agents such as ferric chloride, potassium ferricyanide, and silver nitrate, it is readily decomposed, yielding  $\beta$ -naphthaquinone and methylethylamine, the latter being isolated and identified by means of its acid oxalate (m. p. 152—153°):

0.1243 gave 0.1849  $\text{CO}_2$  and 0.0848  $\text{H}_2\text{O}$ .  $\text{C} = 40.6$ ;  $\text{H} = 7.6$ .

$\text{C}_3\text{H}_9\text{N}, \text{C}_2\text{H}_2\text{O}_4$  requires  $\text{C} = 40.3$ ;  $\text{H} = 7.4$  per cent.



Fractions III and IV were combined, and further fractionated under 40 mm. pressure. In this way, some methylethyl- $\alpha$ -amino- $\beta$ -naphthol was removed, and a fraction boiling at 213—223°, was converted into the *sulphocamphylate*, which crystallised from water in clusters of needles. This salt, which contained one molecule of water, when slowly heated, melted at 196°:

0.4468 lost, at 110°, 0.0164  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 3.6$ .

$\text{C}_{13}\text{H}_{13}\text{ON}, \text{C}_9\text{H}_{14}\text{O}_5\text{S}, \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.0$  per cent.

0.4085 anhydrous salt gave 0.2201  $\text{BaSO}_4$ .  $\text{S} = 7.4$ .

$\text{C}_{13}\text{H}_{13}\text{ON}, \text{C}_9\text{H}_{14}\text{O}_5\text{S}$  requires  $\text{S} = 7.4$  per cent.

The salt, when finally recrystallised from a mixture of alcohol and ether, separated in glistening needles and readily yielded *N*-methyl- $\beta$ -naphthomorpholine, the latter distilling at 220—222°, under 40 mm. pressure. It is a light yellow, viscid oil, having a blue fluorescence and a pleasant odour recalling that of its analogue *N*-methylphenomorpholine; it is quite insoluble in caustic alkalis, and is perfectly stable on exposure to air:

0.1262 gave 0.3624  $\text{CO}_2$  and 0.0754  $\text{H}_2\text{O}$ .  $\text{C} = 78.3$ ;  $\text{H} = 6.6$ .

$\text{C}_{13}\text{H}_{13}\text{ON}$  requires  $\text{C} = 78.4$ ;  $\text{H} = 6.5$  per cent.

Its solution in absolute alcohol gives, with ferric chloride, an intense bluish-green coloration. When sodium nitrite is added to its solution in dilute hydrochloric acid, a deep Prussian-blue colour is developed.

Its *methiodide* formed needles crystallising from a mixture of alcohol and ether, and melting at  $163\text{--}164^\circ$  with loss of methyl iodide:

0.1511 gave 0.2718  $\text{CO}_2$  and 0.0682  $\text{H}_2\text{O}$ .  $\text{C} = 49.1$ ;  $\text{H} = 5.0$ .

$\text{C}_{14}\text{H}_{16}\text{ONI}$  requires  $\text{C} = 49.2$ ;  $\text{H} = 4.7$  per cent.

The authors intend to pursue the line of investigation indicated in the introduction, by preparing and reducing other morpholone derivatives.

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## LXXVIII.—*The Bases contained in Scottish Shale Oil.* *Part II.*

By FREDERIC CHARLES GARRETT and JOHN ARMSTRONG SMYTHIE.

THE examination of these bases has been continued, the fractions boiling between  $164^\circ$  and  $180^\circ$  being treated with mercuric chloride in much the same way as the fractions of lower boiling point (Trans., 1902, 81, 449); the results, however, have been disappointing, and although more than 400 grams of the mixed bases were examined, only two substances were isolated in a state of purity. Several of the less volatile bases form oily mercurichlorides, which solidify only after a long time, crystallisation being incomplete in some cases after an interval of several months; it is obviously impossible to obtain these substances reasonably pure even by repeated precipitation, whilst in other cases, where crystalline compounds were obtained, the very numerous recrystallisations which were needed caused great loss of material, and did not always result in the production of pure substances. Attempts were therefore made to effect a more perfect separation by using platinic chloride in place of the mercury salt, but without success; and the use of picric acid proved equally unsatisfactory.

### 2 : 4 : 6-Trimethylpyridine (*s*-Collidine).

2 : 4 : 6-Trimethylpyridine is by far the most abundant substance in these fractions, and as comparatively large quantities were obtained in a state of great purity, we were able to redetermine the boiling point and other constants given in our former communication; all these were confirmed, except that the boiling point as determined with a new short stem thermometer, certified at the Berlin Reichsan-



stalt, was found to be  $171^{\circ}$  (768 mm.) instead of  $170.5^{\circ}$  (763 mm.). On comparing two portions of the base, prepared from different fractions, a difference in boiling point of only  $0.2^{\circ}$  was found, showing that both specimens must have been very pure.

The aurichloride was easily obtained in long, yellow, hair-like crystals melting about  $53^{\circ}$ , and apparently containing one molecule of water of crystallisation; it is difficult to obtain an exact reading, however, for as soon as the crystals are dry they begin to effloresce, exposure to the air of the laboratory for a few hours rendering them quite anhydrous, the melting point rising to  $112^{\circ}$ . Many analyses were made of which the following are typical:

0.3244 lost 0.0110 at  $95^{\circ}$ , and yielded 0.1336 Au.  $H_2O = 3.39$ ; Au (in the hydrated salt) = 41.2; (in the anhydrous) = 42.63.

0.3675 lost 0.0085 at  $95^{\circ}$ , and yielded 0.1530 Au.

$H_2O = 2.31$  per cent.; Au (in the hydrated salt) = 41.63; (in the anhydrous) = 42.62.  $C_8H_{10}N, HAuCl_4, H_2O$  requires  $H_2O = 3.76$  and Au = 41.18. In the anhydrous salt, Au = 42.74 per cent.

The aurichloride is soluble in about 40 parts of boiling, and in about 350 parts of cold water; the solution on boiling sometimes yields small quantities of a substance forming small, lemon-yellow needles, which are almost insoluble in water, and melt at about  $178^{\circ}$ . The conditions under which this salt is formed were not apparent, and attempts to prepare it in quantity failed, so that full analyses could not be made. There was no loss of weight on heating to  $95^{\circ}$  for two hours:

0.3486 gave 0.1614 Au. Au = 46.31.

0.4069 „ 0.1887 Au. Au = 46.12.

It is conceivable that this might be  $C_8H_{10}N, AuCl_3$ ; (Au = 46.4) although no similar compounds have been observed in other cases.

### 2 : 3-Dimethylpyridine.

From the fraction boiling between  $164^{\circ}$  and  $168^{\circ}$ , about 25 grams of a mercurichloride were obtained in small, colourless needles melting somewhat indefinitely at  $120^{\circ}$ :

0.4074 gave 0.2753 HgS. Hg = 58.25.

$C_7H_9N, HCl, 2HgCl_2$  requires Hg = 58.4 per cent.

From this salt 2—3 grams of the base were obtained; it is a liquid lighter than, and insoluble in, water, having a pleasant, aromatic odour, and boiling at  $163$ — $164^{\circ}$  (768 mm.). The platinichloride was

obtained very easily in orange-red crystals melting sharply and decomposing at  $216^{\circ}$ :

0.3490 gave 0.1084 Pt. Pt = 31.07.

$(C_7H_9N)_2, H_2PtCl_6$  requires Pt = 31.24 per cent.

The aurichloride formed yellow, straw-like crystals which melted at  $96^{\circ}$ , and decomposed slowly at about  $225^{\circ}$ ; the amount prepared was too small for a satisfactory analysis:

0.1410 gave 0.0618 Au. Au = 43.83.

$C_7H_9N, HAuCl_4$  requires Au = 44.13 per cent.

About  $1\frac{1}{2}$  grams of the base were oxidised by potassium permanganate, the solution acidified with sulphuric acid, and silver nitrate added, when a gelatinous precipitate was obtained. After removing the silver by hydrogen sulphide, the product, being found to contain potassium, was dried on the water-bath, and boiled with absolute alcohol containing a little hydrochloric acid; the potassium chloride having been filtered off, the filtrate gave a fairly pure acid, which melted and decomposed at about  $229^{\circ}$  and gave a dirty white sublimate. A larger quantity of the acid was therefore heated in a very small test-tube to  $250^{\circ}$ , when a moderate amount of the sublimate was obtained, which after recrystallising from hot water melted at  $229.5^{\circ}$ ; the acid obtained by oxidation should therefore be quinolinic acid, and the sublimate, nicotinic acid. That the former was quinolinic acid was further proved by its giving a yellow colour with ferrous sulphate, and a fine green fluorescence with resorcinol; for comparison, some quinolinic acid was prepared by oxidising quinoline which had been synthesised by Skraup's reaction, and the two acids were found to agree in all respects. Since on oxidation the base is converted into pyridine-2:3-dicarboxylic acid, and is a lutidine, it can only be 2:3-dimethylpyridine, a compound which has not been hitherto described.

The authors have pleasure in acknowledging their indebtedness to the Research Fund Committee of the Society for a grant towards the expense of this work.

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LXXIX.—*Iminoethers Corresponding with Ortho-substituted Benzenoid Amides.*

By GEORGE DRUCE LANDER and FREDERICK TREVOR JEWSON, A.I.C.

PINNER's well-known reaction for the formation of iminoethers of the :NH type, by the addition of the elements of an alcohol to the nitriles, fails either completely or partially with such aryl nitriles as contain a substituent in the *ortho*-position with respect to the cyanogen group (*Ber.*, 1890, 23, 2917, 2952). An attempt has already been made by one of us (*Trans.*, 1901, 79, 695) to prepare *o*-toluiminoethyl ether from the corresponding amide by means of dry silver oxide and ethyl iodide; the reaction, which was carried out in boiling alcoholic solution, resulted in the formation of *o*-toluonitrile.

The present paper contains an account of further experiments, bearing on the formation and properties of some imino-ethers of this type, which have led to the preparation of the hitherto unknown ethyl- and methyl-iminoethers from *o*-chlorobenzamide and *o*-toluamide. Since experiments do not appear to have been made on the formation of the *o*-chlorobenziminoethers, we first satisfied ourselves that Pinner's reaction is not available for the production of these ethers from *o*-chlorobenzonitrile.

Experiments with salicylamide were also started, but, as Pinner (*loc. cit.*) has shown that iminoether formation occurs with *o*-ethoxybenzonitrile to an appreciable extent, they were not continued, after we had found that the results agreed with our other observations, the hydroxy-group also undergoing alkylation (*Trans.*, 1900, 77, 745).

The formation and yield of *ortho*-substituted iminoethers depends on the experimental conditions, for whereas they are not entirely absent from the product of synthesis in boiling alcoholic solution, and although nitriles are present when boiling ethereal solutions are used, yet the proportion of iminoether to nitrile is notably greater in the latter than in the former case. It is unlikely that this difference depends on the higher temperature of the synthesis in alcohol than in ether, for benziminoethyl ether is not changed by boiling with alcohol. We find further that the formation of nitrile occurs also in the synthesis in boiling alcohol of iminoethers which do not contain an *ortho*-substituent, such as the benzimino- and *p*-toluimino-compounds, but to a very much smaller extent than with an *ortho*-derivative.

As regards the mechanism of the formation of nitriles, it is most improbable that it can be regarded as a simple process of dehydration of the amide, and is, we think, dependent on the formation of iminoether and its decomposition in the following way  $R \cdot C(OEt):NH \rightarrow R \cdot C:N +$



HOEt, this change being known to occur on heating. *o*-Toluiminoethyl ether may be distilled unchanged in a partial vacuum, and we are unable to explain why the change in question should occur in the synthetical operation more readily than with the pure substances. Our purpose, however, was to ascertain the relative stability of the compounds with respect to the loss of alcohol, and, although we have never been in possession of sufficient material to determine the relative temperatures of decomposition, the considerably larger proportion of nitrile formed in the synthesis of an *ortho*-iminoether, as compared with that obtained in the *para*-series, indicates, in our opinion, that the decomposition occurs more easily in the case of the *ortho*-compounds.

The results possess some interest, from the theoretical standpoint, in the light of our knowledge of the influence of orientation and substitution on the course of chemical reaction. From the relationship between iminoether and nitrile, expressed by the scheme



it might be expected that the reaction of formation would as an additive process be subject to retardation when an *ortho*-substituent is present, but that the reverse change, which, when formally expressed, consists only in the expulsion of a molecule of alcohol, should be facilitated, as our results indicate, by the same constitutive factor. We are not aware of any illustration of this phenomenon among *ortho*-substituted benzenoid derivatives, but the increase in the ease of anhydride formation which accompanies the successive introduction of alkyl groups in the succinic acid series (Bischoff, *Ber.*, 1891, 24, 1074) presents a closely allied case.

The previously recorded attempt to prepare *o*-toluiminoethyl ether was made in the hope that it would display the same relative stability towards hydrolysis by acids as the *N*-*o*-tolylacetiminoethers,



We find, as a matter of fact, that in this respect *o*-toluiminoethyl ether has a stability greater than that of its *para*-isomeride.

## EXPERIMENTAL.

### *o*-Chlorobenziminoethers.

*o*-Chlorobenziminoethyl Ether.—Having shown that this compound cannot be prepared from the nitrile by Pinner's method, the alkylation of *o*-chlorobenzamide by means of dry silver oxide and ethyl iodide was attempted in alcoholic solution. A solution of 8 grams of the amide in 24 grams of ethyl iodide and 75 c.c. of absolute alcohol

was treated at the boiling temperature with 18 grams of dry silver oxide. After boiling for one and a half hours, a sample of the solution was tested with ethereal hydrochloric acid, when the slight turbidity produced showed that very little base was present. On distilling the product of reaction in a partial vacuum, the main portion passed over between  $129^{\circ}$  and  $132^{\circ}$  under 34 mm. pressure, and solidified to colourless needles fusing at  $42-43^{\circ}$ , and having the other properties of *o*-chlorobenzonitrile.

Dry ether was now employed as a menstruum instead of alcohol, and a mixture of 6 grams of *o*-chlorobenzamide, 18 grams of ethyl iodide, 15 grams of oxide and 150 c.c. of ether was boiled for 4 hours. Dry ethereal hydrochloric acid precipitated the hydrochloride of the desired base from the filtered solution; the yield, however, was poor, about 3 grams of hydrochloride being obtained. After purification by solution in cold alcohol and precipitation with ether, the hydrochloride decomposed with evolution of ethyl chloride at  $105^{\circ}$ , forming *o*-chlorobenzamide melting at  $139^{\circ}$ , and underwent the characteristic ester hydrolysis on warming in aqueous solution. Chlorine was estimated in the ammonium chloride solution remaining after removing, in a current of steam, the ethyl *o*-chlorobenzoate produced on warming the hydrochloride with water:

0.5646 gave 0.3675 AgCl. Cl = 16.1.

$C_6H_4Cl \cdot C(OC_2H_5):NH, HCl$  requires (for 1 mol. Cl) Cl = 16.1 per cent.

*o*-Chlorobenziminomethyl Ether.—*o*-Chlorobenzamide undergoes "anomalous methylation" (compare this vol., 415) when boiled with methyl iodide and dry silver oxide in ethereal solution. Ten grams of amide were employed, the other materials being used in the same proportions as in the foregoing experiment; the boiling was continued for 4 hours. By treatment of the clear solution with ethereal hydrochloric acid, *o*-chlorobenziminomethyl ether hydrochloride was precipitated as an oil which solidified on stirring, and was purified by recrystallisation from alcohol and ether. On observing the melting point in the usual way, the substance, which had previously evolved methyl chloride, melted sharply at  $139^{\circ}$ , this being the melting point of *o*-chlorobenzamide. By introducing specimens into baths at various temperatures, it was found that fusion with decomposition occurs at  $110^{\circ}$  and above that temperature. The compound gave the characteristic hydrolysis and was analysed in the same way as the ethyl homologue:

0.5456 gave 0.3756 AgCl. Cl = 17.0 instead of the calculated Cl = 17.2 per cent.

*o*-Chlorobenzmethylamide, which does not appear to have been previously described, was isolated from the ethereal solution after

separating the iminoether hydrochloride by shaking the liquid with sodium carbonate solution, drying with anhydrous potassium carbonate and evaporating; the residual solid gave a small quantity of *o*-chlorobenzonitrile on extraction with light petroleum, and the remaining solid, after crystallisation from dilute alcohol, formed colourless needles melting constantly at 92—94°. On hydrolysis, these were shown to be *o*-chlorobenzmethylamide by the formation of *o*-chlorobenzoic acid and methylamine:

0.2076 gave 14.7 c.c. moist nitrogen at 12° and 756 mm.  $N = 8.4$ .

$C_6H_4Cl \cdot CO \cdot NH \cdot CH_3$  requires  $N = 8.3$  per cent.

Benzamide also undergoes "anomalous methylation" under conditions similar to those described above for the *o*-chloroamide.

#### *o*-Toluiminoethers.

Some experiments were made with the object of effecting the iminoether synthesis by the action of the respective alkyl iodides on the silver derivative of *o*-toluamide, and *o*-toluiminomethyl ether was prepared in this way.

The silver derivative of *o*-toluamide, precipitated as a light brown, amorphous powder by adding the calculated quantity of pure sodium hydroxide solution to a dilute alcoholic solution of the amide and silver nitrate in molecular proportion, was not obtained in a pure state, since it contained 49.7 per cent. of silver instead of the calculated 44.6, and was probably contaminated with silver oxide, the presence of which did not, however, seem prejudicial to the purpose of synthesis.

The formation of the methyliminoether took place on allowing the dried silver derivative to remain during three days at the ordinary temperature in contact with a solution of methyl iodide in benzene, the mixture being shaken at intervals. The hydrochloride of the iminoether was precipitated from the clear benzene solution and purified by crystallisation from methyl alcohol and ether. On heating, this hydrochloride behaved like *o*-chlorobenziminomethyl ether hydrochloride; it melted at 139° (*o*-toluamide melts at 140—142°), but did not melt when suddenly heated to 105°; at 110°, decomposition was just perceptible, and it fused and decomposed at 115°:

0.1289 gave 0.1017 AgCl.  $Cl = 19.4$ .

$C_6H_4(CH_3) \cdot C(OCH_3) : NH, HCl$  requires  $Cl = 19.1$  per cent.

The amount of iminoether formed in the above manner was very small, less than 1 gram resulting from 19 grams of impure silver derivative. We were not therefore able to observe the formation of either the nitrile or the isomeric substituted amide.



*o*-Toluiminoethyl Ether.—As the main object of this work was to obtain comparative data relating to the formation and behaviour of the *ortho*-substituted iminoethers, parallel experiments were carried out with *p*-toluamide under conditions as nearly as possible comparable with those under which the *ortho*-amide was studied. The alkylation of the two isomeric amides was examined in ethereal and in alcoholic solutions.

*Ethylation of o- and p-Toluamides in Ethereal Solution.*—Ten grams of each amide were boiled with 38 grams of ethyl iodide, 28 grams of dry silver oxide, and 100 c.c. of dry ether for 16 hours, the clear solutions extracted with water and sodium hydroxide solution, and dehydrated with dry potassium carbonate.

The hydrochloride, precipitated from about one-third of the solution of the product from *o*-toluamide, after crystallisation from alcohol and ether, decomposed at 105—106°, solidified and then melted at 139°, and had the other properties of an iminoether hydrochloride:

0.4908 gave 0.3508 AgCl.  $\text{Cl} = 17.7$ .

$\text{C}_6\text{H}_4(\text{CH}_3)\cdot\text{C}(\text{OC}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$  requires  $\text{Cl} = 17.8$  per cent.

In like manner, a portion of the product from *p*-toluamide yielded the hydrochloride of *p*-toluiminoethyl ether, decomposing at 130—131°, solidifying, and then melting at 152°.

The remaining portions of the ethereal solutions were distilled in a partial vacuum, when the product from the *ortho*-isomeride passed over, without sign of decomposition, between 106° and 118° under 20—25 mm. pressure (the boiling point of *p*-toluiminoethyl ether is 116—118° under 21 mm. pressure).

Both distillates possessed the properties of iminoethers, but whereas that from the *para*-amide was practically free from nitrile, giving a clear solution in cold aqueous hydrochloric acid, the product from the *ortho*-amide was only partially soluble in this reagent, the undissolved portion being identified as *o*-toluonitrile. A comparative estimation of the relative proportions of iminoether and nitrile was made by precipitating and weighing the hydrochlorides from solutions of the same strength in ether and light petroleum; the product from the *ortho*-amide gave a quantity of hydrochloride corresponding with 67 per cent., whilst the hydrochloride obtained from the *para*-isomeride corresponded with 95 per cent. of iminoether.

The stability with regard to hydrolysis by means of aqueous hydrochloric acid was compared by dissolving, at the same moment, 0.3 gram each of *o*- and *p*-toluiminoethyl ether hydrochlorides in 20 c.c. of water at the laboratory temperature. A turbidity, due to the formation of ester, appeared in the solution of *para*-salt after 40 minutes, and in that of *ortho*-salt after 1½ hours, the latter compound dis-

playing, as was anticipated, greater stability in respect to this decomposition.

*Ethylation of o- and p-Toluamides in Alcoholic Solution.*—The reaction was carried out in each instance with 10 grams of amide and the corresponding proportions of oxide and iodide, 75 c.c. of alcohol being added, and the boiling continued for 3 hours. The products were extracted with ether, the extracts being treated similarly to those described above, and distilled in a partial vacuum. Both distillates contained iminoether mixed with a proportion of nitrile which was larger than that found in the 'ether' synthesis.

The amounts of iminoether were determined in each sample by gently warming for a few moments with an excess of  $N/10$  hydrochloric acid, and determining the amount of acid neutralised.

0.2633 *ortho*-product required 2.2 c.c.  $N/10$  HCl, corresponding with 13.6 per cent. of iminoether.

0.2093 *para*-product required 9.0 c.c.  $N/10$  HCl, corresponding with 70.0 per cent. of iminoether.

The expense incurred in this investigation was defrayed by a grant from the Research Fund Committee of the Chemical Society.

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# LXXX.—*The Synthesis of $\alpha\alpha\gamma$ -Trimethylglutaric Acid, of the cis- and trans-Modifications of $\beta$ -Hydroxy- $\alpha\alpha\gamma$ -Trimethylglutaric Acid, and of $\alpha\alpha\gamma$ -Trimethylglutaconic Acid.*

By W. H. PERKIN, jun., and ALICE E. SMITH, B.Sc., 1851 Exhibition Scholar of University College, Bangor.

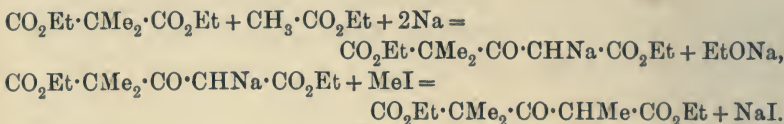
IN a paper published at the commencement of this year (this vol., 8) we described a new method of synthesising  $\alpha\alpha$ -dimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and during the course of this research we were able to isolate in a pure condition the *cis*- and *trans*-modifications of  $\alpha\alpha$ -dimethylglutaconic acid and thus to remove a considerable amount of confusion which had arisen in connection with the identity of these acids. Shortly after these results had been described, E. E. Blaise (*Compt. rend.*, 1903, 136, 381) published an account of an investigation on the  $\alpha\alpha$ -dimethylglutaconic acids, in which he confirms our view that the *cis*-modification of this acid melts at  $135^\circ$  and his description of the liquid anhydride of this acid and of

the anilic acid agrees well with ours. At a later date (*ibid.*, 1903, 136, 692), and still apparently in ignorance of the fact that we had already investigated this matter, he describes the *trans*-modification of  $\alpha\alpha$ -dimethylglutaconic acid, and to this he gives the melting point  $163^\circ$ , but this is much too low, since the pure substance melts at  $172^\circ$ .

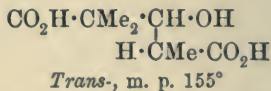
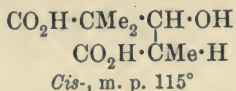
As the method of synthesis which we employed had proved to be of value in the case of the  $\alpha\alpha$ -dimethylglutaconic acids and  $\alpha\alpha$ -dimethylglutaric acid, it occurred to us that it would be interesting to extend our investigation to the trimethylglutaconic acids and trimethylglutaric acid, and we wish now to give a short account of the results which we have obtained in carrying out this work.

A mixture of ethyl dimethylmalonate and ethyl acetate is readily acted on by sodium, yielding the sodium compound of ethyl  $\alpha\alpha$ -dimethylacetonedicarboxylate, and if this is treated with methyl iodide, a methyl group is introduced in the place of the metal and *ethyl  $\alpha\alpha$ -trimethylacetonedicarboxylate* is formed.

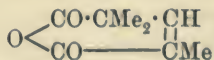
Expressed in the simplest manner, these reactions may be represented thus:



When ethyl  $\alpha\alpha$ -trimethylacetonedicarboxylate is reduced with sodium amalgam, it yields a mixture of two isomeric acids which melt at  $115^\circ$  and  $155^\circ$ , and are obviously the stereoisomeric modifications of  *$\beta$ -hydroxy- $\alpha\alpha$ -trimethylglutaric acid*:



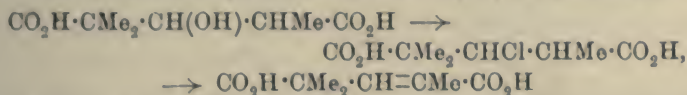
The *trans*-configuration is given to the acid melting at  $155^\circ$ , not only because of its higher melting point, but also because, under reduced pressure, it distils to a large extent without decomposition, whereas the more fusible acid is decomposed, on distillation, with elimination of water and formation of a neutral crystalline substance,  $\text{C}_8\text{H}_{10}\text{O}_3$  (m. p.  $88^\circ$ ), which is probably the anhydride of *cis- $\alpha\alpha$ -trimethylglutaconic acid*:



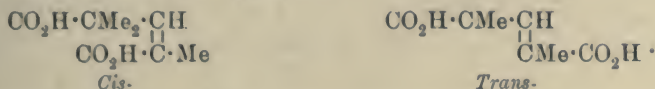
This difference in the behaviour of the two modifications is readily understood if the above configurations are assigned to them.



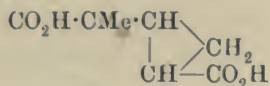
It is curious that both modifications of the hydroxy-acid, when treated successively with phosphorus pentachloride and diethylaniline, should lead to the same  $\alpha\alpha\gamma$ -trimethylglutaconic acid melting at  $150^\circ$ ,



since it was to be expected that each would yield the unsaturated acid with the corresponding configuration :



That the acid melting at  $150^\circ$  is unsaturated, and not a trimethylene derivative having the formula :



(Trans., 1897, 71, 1176), is shown by the fact that it readily reduces permanganate, and, when treated with bromine, is converted into  $\beta\gamma$ -dibromo- $\alpha\alpha\gamma$ -trimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CBrMe}\cdot\text{CO}_2\text{H}$ . There can be little doubt that the acid melting at  $150^\circ$  is the *trans*-modification of  $\alpha\alpha\gamma$ -trimethylglutaconic acid, since, on distillation, it shows no tendency to form an anhydride.

The anhydride of the *cis*-modification is in all probability the neutral substance,  $\text{C}_8\text{H}_{10}\text{O}_3$ , melting at  $88^\circ$  (see above), which is produced when *cis*-hydroxytrimethylglutaric acid is distilled, but, unfortunately, we have so far not had enough material to conclusively demonstrate this interesting point. It may however be mentioned that, in the case of the  $\alpha\alpha$ -dimethylglutaconic acids, the *cis*-modification yields an anhydride, whereas the *trans*-modification shows no tendency to undergo decomposition in this way (Trans., 1902, 81, 256).

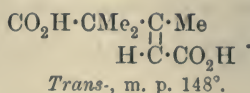
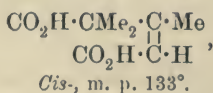
The  $\alpha\alpha\gamma$ -trimethylglutaconic acids described in the present paper are isomeric with the  $\alpha\alpha\beta$ -trimethylglutaconic acids,



which Perkin and Thorpe (Trans., 1897, 71, 1182) had previously obtained during the course of their investigations on the synthesis of *i*-camphoronic acid. This glutaconic acid also exists in two modifications melting at  $133^\circ$  and  $148^\circ$ ; the former yields an anhydride (m. p.  $107^\circ$ ), whereas the latter does not.

The isomerism of these acids was not understood at the time, but in view of the results described in this and in our previous communication

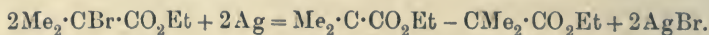
there can now be no doubt that these two acids are the stereoisomeric modifications :



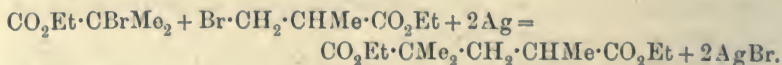
It is very interesting to note that the anhydride of the *cis*-acid crystallises from water unchanged, a behaviour also observed in the case of the anhydride,  $\text{C}_8\text{H}_{10}\text{O}_3$  (m. p.  $88^\circ$ , see above), and which is supposed to be the anhydride of *cis-aay*-trimethylglutaconic acid.

Not only by treatment with phosphorus pentachloride and diethyl-aniline, but also when simply boiled with hydriodic acid and amorphous phosphorus, both the *cis*- and *trans*-modifications of  $\beta$ -hydroxy-aay-trimethylglutaric acid are converted into *trans-aay*-trimethylglutaconic acid and this seems to show that the *cis*-modification of this latter acid is converted with exceptional ease by the action of acids into the *trans*-modification. There appears to be no tendency for the *trans*-trimethylglutaconic acid to be reduced to the corresponding aay-trimethylglutaric acid by the large excess of hydriodic acid employed in these experiments, and indeed it exhibits an exceptional resistance to reducing agents. Ultimately, however, by employing alcohol and sodium in large excess, we were able to reduce it and thus obtained aay-trimethylglutaric acid in glistening crystals melting at  $97-98^\circ$ .

This interesting acid (m. p.  $97-98^\circ$ ) was first prepared by Hell and Wittekind (*Ber.*, 1874, 7, 320 ; compare Hell and W. Mayer, *Ber.*, 1889, 22, 48 ; also Hell and Rothberg, *ibid.*, 60) by the action of silver on ethyl bromoisobutyrate and considered by them to be tetramethylsuccinic acid, the reaction being supposed to take place as follows :

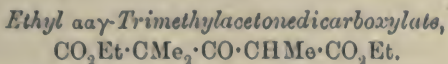


Auwers and Victor Meyer (*Ber.*, 1890, 23, 295) subsequently showed that the acid having this melting point is aay-trimethylglutaric acid and not tetramethylsuccinic acid, and they explained its formation in the following way. During the reaction, part of the ethyl bromoisobutyrate decomposes into hydrogen bromide and ethyl methacrylate and these then recombine to form ethyl  $\beta$ -bromoisobutyrate. The silver then reacts with the mixture of ethyl  $\alpha$ - and  $\beta$ -bromobutyrate now present, to form ethyl aay-trimethylglutarate :



This acid does not appear to have been obtained by any process other than the above rather complicated reaction, and thus the

synthesis which we describe in this paper is a valuable contribution to the nature of the substance.



In preparing this ester, 75 grams of ethyl dimethylmalonate and 70 grams of carefully purified ethyl acetate are dissolved in dry benzene and heated with 32.4 grams of finely divided sodium until the metal has dissolved, which is usually the case after about eight hours. About 200 grams of methyl iodide are then added and the flask, which is well cooled before and during the addition, should be attached to a reflux condenser with a rapid stream of water as the mixture soon becomes hot and boils vigorously. When the reaction has slackened, the flask is heated on a water-bath for two hours, water is then added, and the product extracted with ether. The ethereal solution is washed with water several times, in order to remove alcohol, dried, the ether distilled off, and the remaining oil repeatedly fractionated. A considerable quantity of a colourless oil was thus obtained which distilled at 195—197° (100 mm.) and, on analysis gave the following results :

0.1681 gave 0.3573  $\text{CO}_2$  and 0.1192  $\text{H}_2\text{O}$ .  $\text{C} = 58.0$  ;  $\text{H} = 7.9$ .

$\text{C}_{12}\text{H}_{20}\text{O}_5$  requires  $\text{C} = 59.0$  ;  $\text{H} = 8.2$  per cent.

Although this analysis is not very satisfactory, the subsequent examination of this oil proves conclusively that it consists of *ethyl trimethylacetonedicarboxylate*. This is a stable substance which appears to distil under the ordinary pressure with only slight decomposition ; its alcoholic solution gives a deep violet coloration with ferric chloride.

*Reduction of Ethyl Trimethylacetonedicarboxylate. Formation of the cis- and trans-Modifications of  $\beta$ -Hydroxy- $\alpha\alpha\gamma$ -trimethylglutaric Acid,*  
 $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}.$

The fraction of the oil boiling at 194—200° (100 mm.) was dissolved in 10 times its volume of alcohol, an equal volume of water was then added and the solution transferred to a porcelain beaker surrounded with ice and fitted with a mechanical stirrer. A large excess of sodium amalgam was then gradually added, carbon dioxide being passed through the liquid during the whole operation, and after 48—60 hours and as soon as a small quantity, extracted with ether, gave no coloration with ferric chloride, the whole was acidified with excess of hydrochloric acid,\* separated from the mercury and evapor-

\* Sometimes an oil was deposited when the product was acidified and when this was the case it was separated mechanically and employed in subsequent reductions.



ated to dryness. The dry mass was mixed with sand and extracted with pure ether in a Soxhlet apparatus; the extract when dried over calcium chloride and evaporated yielded a viscid syrup, which, after some days, became almost solid. On grinding the resulting brown mass with dry ether, about three-fourths dissolved, leaving a crystalline residue, which was collected, washed with dry ether, and dissolved in a large quantity of the warm solvent. The solution, when evaporated to a small bulk, slowly deposited hard, crystalline crusts on the sides of the flask; these consisted of the pure *trans*-hydroxy-acid:

0.1770 gave 0.3259 CO<sub>2</sub> and 0.1176 H<sub>2</sub>O. C=50.3; H=7.4.

0.1093 „ 0.2021 CO<sub>2</sub> „ 0.0729 H<sub>2</sub>O. C=50.4; H=7.4.

C<sub>8</sub>H<sub>14</sub>O<sub>5</sub> requires C=50.5; H=7.4 per cent.

*trans*-β-Hydroxy-αγ-trimethylglutaric acid melts at 154–156°, softening at a slightly lower temperature; it is sparingly soluble in ether, chloroform, benzene, or light petroleum, but dissolves very readily in water or alcohol. Its solution in sodium carbonate does not decolorise permanganate in the cold, and even on boiling oxidation takes place only very slowly. When rapidly heated in small quantities under 50 mm. pressure, it gives off carbon dioxide, and an oil distils which, on cooling, partially solidifies, and has the penetrating odour of a higher fatty acid. The distillate was dissolved in a small amount of water, the solution evaporated to a small bulk and mixed with an equal volume of hydrochloric acid. After two days, warty groups of crystals had separated which were collected, and found to consist of unchanged *trans*-hydroxy-acid melting at 152–154°.

It is thus evident that, when rapidly heated under reduced pressure, this acid distils to a large extent unchanged, a behaviour which is very seldom shown by β-hydroxy-acids.

The ethereal mother liquors from the *trans*-acid were evaporated and the residue left over sulphuric acid in a vacuum desiccator until crystallisation, which soon set in, was complete, the semi-solid mass being then spread on porous porcelain. After several days, the hard residue was treated at the pump with dry ether, which dissolved the *cis*-acid, leaving undissolved a trace of the *trans*-acid. The ethereal extract was then evaporated and the residue washed with hot benzene and dissolved in a large quantity of boiling toluene, from which it separated, on cooling, as a hard, crystalline crust. By fractionally crystallising this from toluene the *cis*-hydroxy-acid was obtained pure as a colourless, crystalline powder melting at 115°:

0.1875 gave 0.3464 CO<sub>2</sub> and 0.1252 H<sub>2</sub>O. C=50.4; H=7.4.

C<sub>8</sub>H<sub>14</sub>O<sub>5</sub> requires C=50.5; H=7.4 per cent.

*cis*-β-Hydroxy-αγ-trimethylglutaric acid is readily soluble in ether,

water, and alcohol, but sparingly so in benzene, light petroleum, and chloroform; its solution in sodium carbonate is stable towards permanganate. When this acid is distilled under the ordinary pressure, a large amount of carbon dioxide and water vapour is given off, and an oil distils at about  $200-210^\circ$  which smells strongly of a fatty acid and, on cooling, becomes semi-solid. In contact with porous porcelain the oily impurity is soon removed, leaving a white, crystalline mass which readily separates from light petroleum (in which it is very sparingly soluble in the cold) in colourless, feathery needles, which melt at  $87-88^\circ$ :

0.1376 gave 0.3143  $\text{CO}_2$  and 0.0855  $\text{H}_2\text{O}$ .  $\text{C} = 62.3$ ;  $\text{H} = 6.9$ .

$\text{C}_8\text{H}_{10}\text{O}_3$  requires  $\text{C} = 62.3$ ;  $\text{H} = 6.5$  per cent.

This substance is insoluble in cold water, and, on warming, it first melts and then gradually passes into solution, and, if rapidly cooled, part of it separates unchanged in feathery needles melting at  $88^\circ$ . Unfortunately, the amount of substance at our disposal was so small that we were unable to investigate the nature of the acid present in the mother liquors. The substance (m. p.  $88^\circ$ ) dissolves only very slowly in sodium carbonate, and the solution reduces permanganate in the cold. It is suggested in the introduction that this substance,  $\text{C}_8\text{H}_{10}\text{O}_3$ , is probably the anhydride of *cis*- $\alpha\alpha\gamma$ -trimethylglutaconic acid.

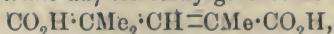
*Formation of trans- $\alpha\alpha\gamma$ -Trimethylglutaconic Acid from the cis- and trans-Modifications of  $\beta$ -Hydroxy- $\alpha\alpha\gamma$ -Trimethylglutaric Acid.*

*Method I. By means of Phosphorus Pentachloride and Diethylaniline.*  
—The *trans*-hydroxy-acid (3 grams) was heated with 10 grams of phosphorus pentachloride for half an hour on the water-bath and then boiled for 15 minutes on the sand-bath, and the liquid cautiously added to a large excess of absolute alcohol. When quite cold, the whole was mixed with water and the heavy chloro-ester extracted with ether; the ethereal solution was well washed until free from alcohol, dried over calcium chloride and evaporated, the residue being then heated to boiling for 15 minutes with twice its volume of diethylaniline. The product was mixed with ether and excess of dilute hydrochloric acid, the ethereal solution separated, evaporated, and the residue hydrolysed by boiling with excess of methyl-alcoholic potash; water was then added and the solution evaporated until free from methyl alcohol. On acidifying and extracting with ether, a solid acid was obtained which, when crystallised from water with the aid of animal charcoal, formed colourless, glistening needles melting at  $149-150^\circ$ :

0.1275 gave 0.2601  $\text{CO}_2$  and 0.0811  $\text{H}_2\text{O}$ .  $\text{C} = 55.6$ ;  $\text{H} = 7.1$ .]

$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.8$ ;  $\text{H} = 7.0$  per cent.

This substance is *trans*- $\alpha\alpha$ -trimethylglutaconic acid,



the properties of which are given below. An exactly similar experiment was then made with the *cis*-hydroxy-acid, with the unexpected result that, in this case also, an acid was obtained which melted at  $150^\circ$ , and, on analysis, proved to be *trans*- $\alpha\alpha$ -trimethylglutaconic acid identical with the acid obtained from the *trans*-hydroxy-acid:

0.1591 gave 0.3257  $\text{CO}_2$  and 0.1004  $\text{H}_2\text{O}$ .  $\text{C} = 55.8$ ;  $\text{H} = 7.0$ .

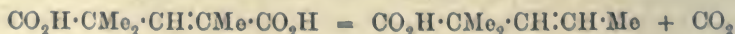
$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.8$ ;  $\text{H} = 7.0$  per cent.

*Method II. By Reduction with Hydriodic Acid.*—In the first experiment, the *cis*-hydroxy-acid (3 grams) was warmed on the water-bath for one and a half hours with 25 c.c. of hydriodic acid (sp. gr. 1.7) and one gram of amorphous phosphorus, and then heated to boiling on the sand-bath for two hours.

The liquid was cooled, filtered, saturated with ammonium sulphate, and repeatedly extracted with ether, when, after washing with a little dilute sulphurous acid to remove traces of iodine and distilling off the ether, a yellow oil was obtained which solidified on cooling. After removing oily mother liquor by contact with porous porcelain, the residue crystallised from water in colourless needles, which melted at  $149$ – $150^\circ$ , and, on careful comparison, this acid was found to be identical with the *trans*- $\alpha\alpha$ -trimethylglutaconic acid which had been obtained with the aid of phosphorus pentachloride as described above. The *trans*-hydroxy-acid was next treated with hydriodic acid in exactly the same way, and this also yielded *trans*- $\alpha\alpha$ -trimethylglutaconic acid melting at  $148$ – $150^\circ$ .

Probably the best way of preparing the latter acid is to treat the mixed *cis*- and *trans*-hydroxy-acids with phosphorus pentachloride and diethylaniline in the manner described at the beginning of this section.

*trans*- $\alpha\alpha$ -Trimethylglutaconic acid is sparingly soluble in benzene and light petroleum, but readily so in water, from which it separates in glistening needles melting at  $150^\circ$ . It behaves like an unsaturated acid, since its solution in sodium carbonate rapidly decolorises permanganate in the cold. When heated in small quantities, some carbon dioxide is evolved, and an oil distils, which, on cooling, partly solidifies. If this distillate is digested with light petroleum, an unsaturated oil, smelling strongly of a fatty acid, is extracted, which is doubtless crotonyldimethylacetic acid, produced according to the equation:

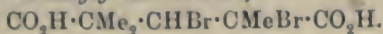


(compare *Trans.*, 1902, 81, 256), but the quantity was too small for examination. The solid portion, insoluble in light petroleum, crystallised from water in colourless needles which melted at  $148$ – $150^\circ$ , and



consisted of unchanged *trans-ααγ*-trimethylglutaconic acid. From this it follows that, when heated in small quantities, this acid is, to a large extent, volatile without decomposition.

*βγ*-Dibromo-*ααγ*-trimethylglutaric Acid,



When *trans-ααγ*-trimethylglutaconic acid is exposed to the action of dry bromine vapour for 2 days, and the excess of bromine then removed by leaving the gummy product over powdered potash in a vacuum desiccator, an ochre-coloured substance is obtained, which crystallises from formic acid (sp. gr. 1.22) in needles, and melts and decomposes at 205—207°. The analysis shows that this substance is the dibromo-acid having the above formula :

0.2062 gave 0.2350 AgBr. Br = 48.4.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Br}_2$  requires Br = 48.2 per cent.

When this dibromo-acid is heated in a test-tube, it evolves bromine and hydrogen bromide, and an oil distils which solidifies on cooling, no residue being left in the tube.

*ααγ*-Trimethylglutaric Acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ .

As stated in the introduction, *trans-ααγ*-trimethylglutaconic acid is reduced with difficulty, and the only way in which the reduction could be carried out was by means of sodium and alcohol.

The acid was dissolved in alcohol, the solution heated to boiling in a large flask connected with a wide reflux condenser, and then a very large excess of sodium added as quickly as possible. The mass was dissolved in water, evaporated until free from alcohol, acidified, and extracted with ether, but as the residue from the ether still contained trimethylglutaconic acid, the reduction with sodium and alcohol was repeated. The acid from the second reduction was fractionally crystallised from water with the aid of animal charcoal, and in this way, glistening crystals were obtained, which melted at 97—98°, and consisted of *ααγ*-trimethylglutaric acid. Auwers and Victor Meyer (*Ber.*, 1890, 23, 300) give 97° as the melting point of *ααγ*-trimethylglutaric acid :

0.1026 gave 0.2053  $\text{CO}_2$  and 0.0757  $\text{H}_2\text{O}$ . C = 54.5 ; H = 8.2.

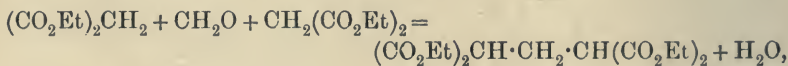
$\text{C}_8\text{H}_{14}\text{O}_4$  requires C = 55.1 ; H = 8.0 per cent.

The slight deficiency in carbon is due to the substance containing a trace of ash which was not removed by recrystallisation.

LXXXI.—*Hexamethyleneoctocarboxylic Acid and the cis- and trans-Modifications of Hexamethylenetetracarboxylic Acid (Hexahydropyromellitic Acid).*

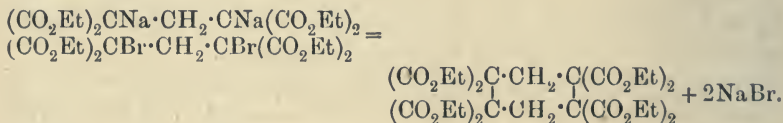
By T. W. 'D. GREGORY and W. H. PERKIN, jun.

DURING the course of a series of experiments on the condensation of ethyl malonate with formaldehyde (Haworth and Perkin, *Trans.*, 1898, 73, 330; Bottomley and Perkin, 1900, 77, 294; compare Knoevenagel, *Ber.*, 1894, 27, 2345), the observation was made that ethyl propanetetracarboxylate, which, in certain circumstances, is the principal product of the reaction

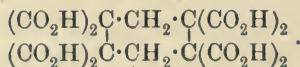


is readily acted on by bromine with the formation of *ethyl dibromopropanetetracarboxylate*,  $(\text{CO}_2\text{Et})_2\text{CBr}\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{Et})_2$ .

When this ester is digested with the disodium compound of ethyl propanetetracarboxylate, sodium bromide is immediately eliminated and an almost quantitative yield of *ethyl hexamethyleneoctocarboxylate* is obtained,



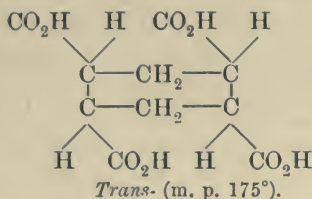
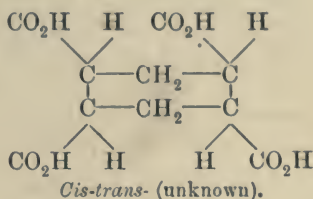
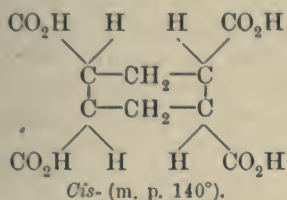
This interesting ester is a beautifully crystalline substance which melts at 46° and which, when boiled with concentrated hydrochloric acid, is almost quantitatively hydrolysed with the formation of the corresponding *hexamethyleneoctocarboxylic acid*,



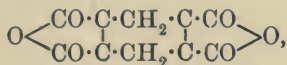
That this acid should be formed in this way is certainly remarkable, because esters which contain the grouping  $\text{:C}(\text{CO}_2\text{Et})_2$ , when digested with concentrated hydrochloric acid, are not only hydrolysed but also lose carbon dioxide, the above group becoming  $\text{:CH}\cdot\text{CO}_2\text{H}$ . It is difficult to understand why, in the case of this ester, which contains no less than four of these  $\text{:C}(\text{CO}_2\text{Et})_2$  groupings, there should be no elimination of carbon dioxide on hydrolysis with boiling hydrochloric acid.

Hexamethyleneoctocarboxylic acid melts at 218° with rapid evolution of carbon dioxide and formation of a mixture of the *trans*-

modification of *hexamethylenetetra-carboxylic acid* (hexahydropyromellitic acid) and the double anhydride of the *cis*-modification of the same acid. Since this acid contains two pairs of asymmetric carbon atoms, it may, of course, exist in the following modifications :



The above mentioned double anhydride of the *cis*-acid, which has the constitution



melts at 60° and behaves normally on treatment with aniline, yielding a double anilic acid from which the corresponding double anil is obtained by the action of heat. It is readily converted into the *cis*-acid (m. p. 139—140°) by boiling with water. Experiments which were instituted with the object of converting this *cis*-acid into the *trans*-modification by heating with hydrochloric acid were unsuccessful owing to decomposition taking place before the temperature necessary for the isomeric change had been reached.

On the other hand, the *trans*-acid, when heated with acetic anhydride at 200° and then distilled, yields large quantities of the anhydride of the *cis*-acid, and there can thus be no doubt that these two acids are stereoisomeric modifications of hexamethylenetetra-carboxylic acid. It would have been interesting to have isolated the *cis-trans*-modification of this acid which is represented above, but, although many experiments were carried out with the object of obtaining this form, it was found impossible to isolate it in a pure condition. Attempts were also made to remove the six hydrogen atoms from the anhydride of the *cis*-acid by treatment first with bromine and then with caustic potash, in the hope of thus synthesising pyromellitic acid, but the decomposition proceeded in another direction and we were unable to isolate even traces of this acid.



*Ethyl Dibromopropanetetra-carboxylate,*  
 $(\text{CO}_2\text{Et})_2\text{CBr}\cdot\text{CH}_2\cdot\text{CBr}(\text{CO}_2\text{Et})_2$ .

In order to obtain a satisfactory yield of this bromo-ester, it is essential that the ethyl propanetetra-carboxylate employed shall be carefully purified by repeated fractionation, as small quantities of impurity very much hinder the solidification of the bromo-ester. The pure ester (30 grams) is dissolved in three times its volume of chloroform and mixed with rather more than the calculated quantity of bromine (35 grams), a trace of iodine is then added, and the whole heated on the water-bath in a reflux apparatus until hydrogen bromide has almost ceased to be evolved, which is usually the case after 6 or 8 hours. Substitution takes place very slowly, especially at first, and is considerably hastened if the flask containing the mixture is exposed to direct sunlight. The product, when washed with dilute sulphurous acid in order to remove hydrogen bromide and excess of bromine, dried over calcium chloride and evaporated, yields an oily residue, which slowly solidifies. The crystals are freed as far as possible from oily mother liquor by contact with porous porcelain, and then recrystallised from dilute methyl alcohol, from which the substance separates in colourless prisms. On analysis:

0.1819 gave 0.1392 AgBr.  $\text{Br} = 32.6$ .

$\text{C}_{15}\text{H}_{22}\text{O}_8\text{Br}_2$  requires  $\text{Br} = 32.7$  per cent.

*Ethyl dibromopropanetetra-carboxylate* melts at  $54-55^\circ$ , and is readily soluble in most organic solvents with the exception of light petroleum, in which it dissolves very sparingly. It is readily acted on by alcoholic potash with the formation of a deep yellow salt, which is at present under investigation. When it is boiled with diethylaniline, a vigorous reaction takes place, the solution rapidly becoming black.

*Ethyl Hexamethyleneoctocarboxylate,*

$$\begin{array}{c} (\text{CO}_2\text{Et})_2\text{C}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2 \\ (\text{CO}_2\text{Et})_2\text{C}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2 \end{array}$$

In preparing this ester, pure ethyl propanetetra-carboxylate (14 grams) is mixed with a solution of sodium (2 grams) in 30 grams of absolute alcohol, and then treated all at once with powdered ethyl dibromopropanetetra-carboxylate (20 grams), the temperature being kept below  $30^\circ$  by cooling with water. The reaction takes place immediately, and quantities of sodium bromide separate in the cold; after a few minutes, the decomposition is completed by heating the mixture for 10 minutes on the water-bath.

When the product is poured into four times its volume of water an

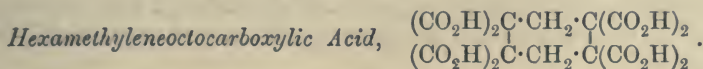
oil separates which quickly solidifies; after about an hour, the precipitate is collected, washed thoroughly with water, spread on porous porcelain, and dried over sulphuric acid. It is then purified by recrystallisation from light petroleum, from which it gradually separates in needles which greatly resemble crystals of sublimed phthalic anhydride and are often several inches in length:

0.1439 gave 0.2870  $\text{CO}_2$  and 0.0868  $\text{H}_2\text{O}$ .  $\text{C} = 54.4$ ;  $\text{H} = 6.7$ .

0.1581 „ 0.3152  $\text{CO}_2$  „ 0.0946  $\text{H}_2\text{O}$ .  $\text{C} = 54.4$ ;  $\text{H} = 6.5$ .

$\text{C}_{30}\text{H}_{44}\text{O}_{16}$  requires  $\text{C} = 54.5$ ;  $\text{H} = 6.6$  per cent.

*Ethyl hexamethyleneoctocarboxylate* melts at  $46^\circ$ , and is readily soluble in alcohol, chloroform, acetic acid, and benzene; it dissolves readily in boiling light petroleum (b. p.  $70-80^\circ$ ), but is sparingly soluble in this solvent in the cold. The ester crystallises best from light petroleum or dilute methyl alcohol, but even from these media it is obtained in crystals with some difficulty, owing to its tendency to separate from warm solvents in the form of an oil. When a small quantity is heated in a test-tube, it distils without any residue and apparently without decomposition, as the colourless distillate solidifies on cooling.



In preparing this acid, the pure ester was heated to boiling in a reflux apparatus with concentrated hydrochloric acid until the oil had entirely dissolved. The solution, when evaporated to a small bulk, slowly deposited a crystalline crust which was collected at the pump, and washed with hydrochloric acid. On concentrating the filtrate, a further crop of crystals was obtained and the concentration of the mother liquors was repeated several times until crystals ceased to separate. Finally, the mother liquors were evaporated nearly to dryness and the semi-solid residue left in contact with porous porcelain until dry. In a quantitative experiment, the total yield of acid obtained from 50 grams of ester was 29 grams, whereas the calculated yield is 33 grams. For analysis, the acid was again crystallised from hydrochloric acid and thus obtained in colourless, glistening crystals:

0.1382 gave 0.1940  $\text{CO}_2$  and 0.0368  $\text{H}_2\text{O}$ .  $\text{C} = 38.3$ ;  $\text{H} = 2.9$ .

0.2073 „ 0.2911  $\text{CO}_2$  „ 0.0540  $\text{H}_2\text{O}$ .  $\text{C} = 38.3$ ;  $\text{H} = 2.8$ .

$\text{C}_{14}\text{H}_{12}\text{O}_{16}$  requires  $\text{C} = 38.5$ ;  $\text{H} = 2.7$  per cent.

*Hexamethyleneoctocarboxylic acid* melts at about  $218-220^\circ$  with rapid decomposition, due to the escape of carbon dioxide and steam. It is sparingly soluble in dry ether, benzene, chloroform, and light

petroleum, but readily soluble in alcohol. It dissolves to almost any extent in water, from which it readily crystallises, if the strong solution is saturated with hydrogen chloride.

*Salts of Hexamethyleneoctocarboxylic Acid.*—The silver salt,  $C_6H_4(CO_2Ag)_8$ , is obtained as a white, caseous, very insoluble precipitate on adding silver nitrate to a slightly alkaline solution of the ammonium salt. This salt explodes on heating, giving a very voluminous mass of carbon, and for this reason considerable difficulty was experienced in obtaining satisfactory results on analysis. The silver was determined by heating the salt with hydrochloric and nitric acids in a sealed tube at  $180^\circ$ , and in determining the carbon and hydrogen, the substance was mixed in the combustion tube with powdered copper oxide:

0.2694 gave 0.1284  $CO_2$  and 0.0154  $H_2O$ . C = 13.0; H = 0.6.

0.2910 „ 0.2571 AgCl. Ag = 66.4.

$C_{14}H_4Ag_8O_{16}$  requires C = 13.0; H = 0.3; Ag = 66.9 per cent.

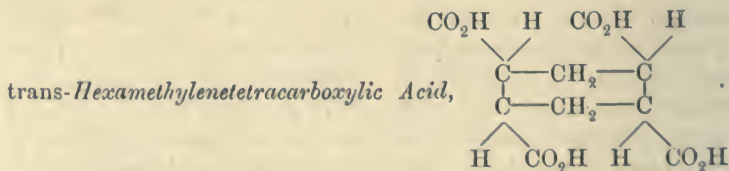
A slightly alkaline solution of the ammonium salt immediately gives, in the cold, caseous precipitates with barium or calcium chloride. When titrated with decinormal caustic soda, using phenolphthalein as the indicator, hexamethyleneoctocarboxylic acid does not neutralise quite the theoretical amount of alkali. Three experiments made with three different preparations of the acid gave the following results:

I. 0.1947 neutralised 0.1394 NaOH = 71.5 per cent.

II. 0.2107 „ 0.1504 NaOH = 71.4 „

III. 0.1956 „ 0.1368 NaOH = 70.0 „

The amount of caustic soda neutralised by an octocarboxylic acid having the formula  $C_{14}H_{12}O_{16}$  is theoretically 73.4 per cent.



When hexamethyleneoctocarboxylic acid, in quantities of not more than 5 grams, is heated in a wide test-tube in a sulphuric acid bath at  $230^\circ$ , much steam and carbon dioxide are given off, and in about ten minutes the frothing has ceased and the decomposition is complete.

The residue, which solidifies on cooling, consists of *trans*-hexamethylenetetracarboxylic acid and the anhydride of the *cis*-modification of the same acid, the latter being present in by far the larger



quantity. In order to separate these two substances, the brown mass is powdered and digested with toluene in which the anhydride dissolves, but in which the *trans*-acid is almost insoluble.

After collecting at the pump and washing with toluene, the grey residue is dried at  $100^{\circ}$  until free from toluene, dissolved in water, and the solution decolorised by boiling with animal charcoal.

The pure *trans*-acid gradually separates in colourless, glistening plates when the concentrated aqueous solution is mixed with an equal volume of hydrochloric acid :

0.1531 gave 0.2593  $\text{CO}_2$  and 0.0677  $\text{H}_2\text{O}$ .  $\text{C} = 46.2$  ;  $\text{H} = 4.9$ .

0.1537 „ 0.2599  $\text{CO}_2$  and 0.0675  $\text{H}_2\text{O}$ .  $\text{C} = 46.1$  ;  $\text{H} = 4.8$ .

$\text{C}_{10}\text{H}_{12}\text{O}_8$  requires  $\text{C} = 46.2$  ;  $\text{H} = 4.6$  per cent.

*trans*-Hexamethylenetetracarboxylic acid melts at  $175^{\circ}$ , and immediately solidifies again a few degrees below this temperature. It is sparingly soluble in benzene, chloroform, and light petroleum, but dissolves readily in alcohol and ether. It is very soluble in water, although to a less extent than the *cis*-acid, and crystallises well from hydrochloric acid, but the crystals are, as a rule, not well defined.

On titration with decinormal caustic soda, using phenolphthalein as the indicator, 0.1977 required, for neutralisation, 0.1214  $\text{NaOH}$ , whereas this amount of a tetrabasic acid,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , should neutralise 0.1216  $\text{NaOH}$ .

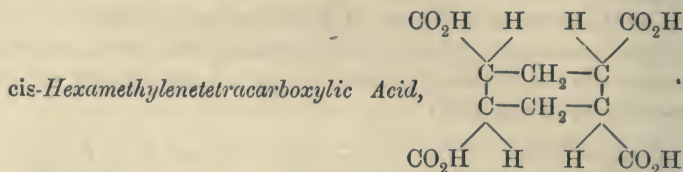
The slightly alkaline solution of the ammonium salt of this acid gives no precipitates with barium or calcium chloride, even on boiling, and in this respect the *trans*-acid differs from the *cis*-acid (p. 787). Zinc sulphate also gives no precipitate in the cold, but, on boiling, a very sparingly soluble salt separates in globular masses resembling starch granules. Mercuric chloride gives no precipitate at first, but the solution soon becomes cloudy, and, on warming, a very sparingly soluble, apparently crystalline, salt separates.

*Conversion of trans-Hexamethylenetetracarboxylic Acid into the cis-Modification.*—When heated by itself, the *trans*-acid distils almost without decomposition and shows only little tendency to pass into the anhydride of the *cis*-acid. If, however, the *trans*-acid is heated in a sealed tube with acetic anhydride at  $200^{\circ}$  for three hours, and the product, after distilling off the acetic acid and excess of acetic anhydride, is distilled under reduced pressure (15 mm.), a considerable quantity of oil passes over, leaving a carbonaceous mass in the retort. The distillate solidifies on cooling, and, after removing the oily mother liquor by contact with porous porcelain and crystallisation from toluene, colourless crystals are obtained which melt at  $60^{\circ}$  and consist of the pure anhydride of the *cis*-acid :

0.1003 gave 0.1967  $\text{CO}_2$  and 0.0344  $\text{H}_2\text{O}$ .  $\text{C} = 53.3$ ;  $\text{H} = 3.8$ .

$\text{C}_{10}\text{H}_8\text{O}_6$  requires  $\text{C} = 53.5$ ;  $\text{H} = 3.6$  per cent.

The identity of this anhydride was further established by converting it into the *cis*-acid, which melted at  $138-140^\circ$ .



The dark brown toluene mother liquors from the purification of the *trans*-acid contain the anhydride of the *cis*-acid.

These were in the first instance digested for an hour with animal charcoal, and after filtering, evaporated to a small bulk, when, on remaining over-night, thick, curiously-shaped, light brown, crystalline masses had separated, and a further crop was obtained from the mother liquors by again treating with animal charcoal and evaporating to a small bulk. This crude anhydride was purified by recrystallising several times from toluene, traces of the *trans*-acid, if present, being always carefully removed by filtration before the anhydride was allowed to separate:

0.1827 gave 0.3558  $\text{CO}_2$  and 0.0637  $\text{H}_2\text{O}$ .  $\text{C} = 53.2$ ;  $\text{H} = 3.8$ .

0.1646 „ 0.3219  $\text{CO}_2$  „ 0.0573  $\text{H}_2\text{O}$ .  $\text{C} = 53.3$ ;  $\text{H} = 3.8$ .

$\text{C}_{10}\text{H}_8\text{O}_6$  requires  $\text{C} = 53.5$ ;  $\text{H} = 3.6$  per cent.

The *anhydride* of *cis*-hexamethylenetetracarboxylic acid melts at about  $60^\circ$ , and is readily soluble in ether but sparingly so in benzene, light petroleum, and chloroform; it is insoluble in cold water, but slowly dissolves in sodium carbonate with effervescence. When heated with resorcinol and a drop of sulphuric acid at  $130^\circ$ , it yields a dark brown mass from which water precipitates an orange-coloured substance exactly like fluorescein in appearance. This dissolves in caustic soda, and if the dark brown solution is thrown into a large quantity of water, an intense fluorescence, indistinguishable from that of fluorescein, is produced.

When warmed with water, the anhydride first melts and then rapidly dissolves, and if the solution is evaporated nearly to dryness, the *cis*-acid separates on cooling in crystalline flakes and sometimes in flat prisms. These were collected on the pump, and purified by recrystallisation from hydrochloric acid:

0.1877 gave 0.3174  $\text{CO}_2$  and 0.0794  $\text{H}_2\text{O}$ .  $\text{C} = 46.1$ ;  $\text{H} = 4.7$ .

0.1325 „ 0.2235  $\text{CO}_2$  „ 0.0560  $\text{H}_2\text{O}$ .  $\text{C} = 46.0$ ;  $\text{H} = 4.7$ .

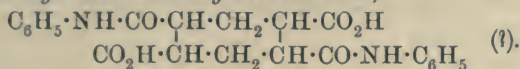
$\text{C}_{10}\text{H}_{12}\text{O}_8$  requires  $\text{C} = 46.1$ ;  $\text{H} = 4.6$  per cent.

*cis-Hexamethylenetetra-carboxylic acid*, when quite pure, melts at about 139—140°, but the exact temperature is ascertained with difficulty owing to the fact that the acid melts to a thick syrup, which only gradually becomes clear. It is excessively soluble in water, and dissolves readily even in concentrated hydrochloric acid; it is, however, sparingly soluble in chloroform, benzene, and light petroleum. On titration with decinormal caustic soda, using phenolphthalein as the indicator, 0.2042 required for neutralisation 0.1245 NaOH, whereas this amount of a tetrabasic acid,  $C_{10}H_{12}O_8$ , should neutralise 0.1256 NaOH.

The salts of the *cis*-acid differ very considerably in solubility from those of the corresponding *trans*-acid (p. 785).

The slightly alkaline solution of the ammonium salt gives no precipitate with calcium chloride in the cold, but, on boiling, a beautifully crystalline and very sparingly soluble calcium salt separates in six-sided plates. Barium chloride also gives no precipitate, in the cold, and, on boiling, the insoluble barium salt gradually crystallises in slender needles. Copper sulphate gives no precipitate, but, on gently warming, a bluish-green, amorphous salt separates; zinc sulphate gives no precipitate, but mercuric chloride and lead acetate immediately produce white precipitates.

*cis-Hexamethylenetetra-carboxydianilic Acid*,



On adding aniline to a solution of the anhydride in benzene, this substance separates at once as a thick syrup which gradually solidifies. It is readily purified by recrystallisation from methyl alcohol, from which it separates, either as a sandy powder consisting apparently of truncated octahedra, or in glistening plates. It melts at about 172°, softening at a slightly lower temperature, and then decomposing vigorously into water and the dianil:

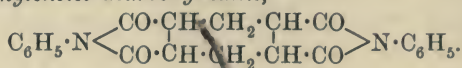
0.2128 gave 13.2 c.c. nitrogen at 20° and 752 mm.  $N = 7.0$ .

$C_{22}H_{22}O_8N_2$  requires  $N = 6.8$  per cent.

This *dianilic acid* is sparingly soluble in benzene, light petroleum, chloroform, and methyl alcohol in the cold, but dissolves moderately readily in the latter solvent on boiling; it dissolves in dilute aqueous caustic potash, and is reprecipitated on the addition of acid.



*cis*-Hexamethylenetetra-carboxydianil,



At 200°, the dianilic acid decomposes rapidly with evolution of steam, and the residue solidifies at once on cooling. By recrystallising from benzene or dilute methyl alcohol, the dianil is readily obtained pure in the form of long, thin needles which melt at 98°:

0.1474 gave 10 c.c. nitrogen at 18° and 757 mm.  $\text{N} = 7.7$ .

$\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_2$  requires  $\text{N} = 7.5$  per cent.

*Attempts to convert cis-Hexamethylenetetra-carboxylic Acid into the trans-Modification.*—When the *cis*-acid dissolved in a small quantity of water is heated with hydrochloric acid at 175° for 1 hour, the solution remains nearly colourless, and, on evaporating to a small bulk, the unchanged acid separates. Several additional experiments were then made at gradually increasing temperatures up to 195°, but at the latter temperature decomposition took place with elimination of carbon dioxide and separation of carbonaceous flocks. On examining the contents of the tubes, which had been heated between 170° and 195°, no indication was observed of any conversion of the *cis*- into the *trans*-modification. The reverse change, namely, the conversion of the *trans*- into the *cis*-modification, is described on p. 785.

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## LXXXII.—*Hydrocyanic Acid in Fodder-plants.*

By J. C. BRÜNNICH.

THE discovery by Messrs. Dunstan and Henry\* of a glucoside "dhurrin," contained in the young plants of the sorghum, which on decomposition in presence of water yields free hydrocyanic acid, is of the greatest importance because this explains the numerous cases of sudden death occurring among cattle fed on immature sorghum.

\* "Cyanogenesis in Plants. II." By Wyndham R. Dunstan and T. A. Henry (*Phil. Trans.*, 1902, Series A, 399).

[Dunstan and Henry have shown that with both *Sorghum vulgare* and *Lotus arabicus* (*Phil. Trans.*, 1901, Series B, 515) the production of hydrocyanic acid increases with the growth of the plant towards maturity and then rapidly diminishes. —EDITOR.]

It becomes very important to ascertain at what periods, and under what conditions of growth, the important fodder-plants belonging to this genus of grasses are most dangerous, and when they may be eaten with impunity.

Veterinary Inspector W. C. Quinnell, in a paper on the "Injurious effects of sorghum on stock," read before the Agricultural Conference, held at Toowoomba, Queensland, on June 11th, 1902, enumerated some of the conflicting statements and theories advanced on this subject under the following heading:

*Circumstances and Conditions under which Sorghum is believed to become Poisonous.*

1. If sorghum is eaten in an immature condition.
2. When sorghum grows rapidly after rainfall.
3. When the plant is stunted by failure of rain or by frost.
4. When sorghum is attacked by insects during an exceptionally dry season.
5. A poisonous mould or fungus is supposed to be the medium of poison.
6. In some parts of India, the plant is said to be poisonous until the rains (monsoons) are over.
7. The poisoning is attributed to the potassium nitrate, which under certain conditions is precipitated in the stems of the plants.
8. Physiological changes in the growth of the plant owing to climatic disturbances, such as want of rain, excess of humidity, damp cloudy weather, or prevalence of extremely variable and unnaturally high temperatures.

In order to test these theories thoroughly, the Queensland Department of Agriculture carried out a series of experiments on an experimental plot in the Brisbane Botanic Garden. This plot, which was exceptionally well situated on the river bank, consisted of a loose, but rather poor, sandy soil. The sorghum varieties "Planter's Friend" or "Imphee," and "Early Amber," and also a variety of Indian corn or maize, were grown in rows 5 feet apart. Some of these rows were left unmanured, and others were manured with sodium nitrate in three applications of 2.5 cwt. per acre each, in order to test the influence of heavy nitrogenous manure. At first the plots had to be watered artificially, but at the end of January, showery weather with high temperatures set in, which continued until the experiments were concluded.

The samples, when cut for analysis, were taken from measured areas, weighed, and quickly disintegrated.

For the estimation of the hydrocyanic acid, 200 grams of the minced fodder were mixed with 200 grams of water, and left to macerate for 20 hours in a well-stoppered bottle at the ordinary temperature. The formation of the free acid generally began in 15 to 30 minutes, as was indicated by a piece of Schönbein-Pagenstecher's test paper suspended from the stopper. At the end of 20 hours, the pulp was quickly pressed through a linen cloth, and the hydrocyanic acid in 100 c.c. of the liquid determined by distillation into a small quantity of water containing about 5 c.c. of decinormal caustic soda solution. In all cases, the hydrocyanic acid was determined volumetrically with decinormal silver nitrate, but a comparison of the volumetric and gravimetric methods showed that the results agreed very closely:

| Percentage of HCN found |                 |
|-------------------------|-----------------|
| volumetrically          | gravimetrically |
| 0.00383                 | 0.00382         |
| 0.01090                 | 0.01082         |
| 0.01170                 | 0.01165         |
| 0.00275                 | 0.00272         |
| 0.00756                 | 0.00749         |

Experiments carried out in order to ascertain whether longer digestion would make any difference in the amounts of hydrocyanic acid liberated, or whether a loss of the acid might take place, gave the following results:

| Percentage of HCN<br>after 20 hours. | Percentage of HCN<br>after 42 hours. | Percentage of HCN<br>after 66 hours. |
|--------------------------------------|--------------------------------------|--------------------------------------|
| 0.0108                               | 0.0102                               | —                                    |
| 0.0349                               | —                                    | 0.0340                               |
| 0.0174                               | 0.0166                               | —                                    |
| 0.0082                               | —                                    | 0.0080                               |

The addition of preservatives during maceration completely stopped the fermentative action. When 1 c.c. of formalin solution was added to the liquid, no trace of hydrocyanic acid was formed, even after a week; chloroform acted similarly.

It was found, on distilling the hydrocyanic acid, that an addition of 2 or 3 c.c. of dilute sulphuric acid slightly increased the amount of hydrocyanic acid obtained, and for this reason the mineral acid was always added before distillation:

| Percentage of HCN<br>distilled with acid. | Percentage of HCN<br>distilled without acid. |
|---|--|
| 0.0276                                    | 0.0252                                       |
| 0.0190                                    | 0.0175                                       |
| 0.0138                                    | 0.0125                                       |



The tables I to III (pp. 793—795) show the results of the numerous analyses, giving the composition of the original green fodder, and also the values (numbers in italics) calculated on the amount of dry substance in the fodder.

In the sorghum varieties, "Imphee" and "Early Amber," the amount of hydrocyanic acid gradually diminishes as the crop matures, but it is impossible to say at what age the crop becomes absolutely safe for use, as this will depend to a large extent on the individual animals, and also on the conditions under which the crop has been grown. It may, however, be safely stated that as soon as the seeds are fully developed the amount of hydrocyanic acid is so much diminished that the fodder will then be innocuous.

Attention must be particularly drawn to the fact that disintegrating, or even sun-drying, the fodder will not eliminate the danger, as is often popularly stated. It will be seen that a disintegrated sample of the "Planter's Friend" had only lost a very small amount of the poison after 40 hours, whilst a sample kept in an open dish contained somewhat less hydrocyanic acid owing to loss by fermentation (Table IV, p. 796).

In all cases, the influence of favourable weather and heavy nitrogenous manuring increases the amount of poisonous glucoside.

Indian corn or maize, in which the presence of the glucoside has not hitherto been suspected, also contains a small amount, which increases up to the flowering stage, and decreases rapidly as soon as the cobs begin to form, but the actual quantity does not become dangerous in ordinary circumstances. No definite relation between the total quantity of nitrogen and the amount of hydrocyanic acid seems to exist.

Samples of the popular fodder plants "Kafir Corn," "Guinea Grass," or *panicum maximum*, and *panicum muticum*, grown in various localities were examined, and they all contained a glucoside yielding hydrocyanic acid.

It will be of the greatest practical importance to test other varieties of sorghum and maizes in order to ascertain which varieties are most dangerous, and which can be used with safety at all stages of growth.

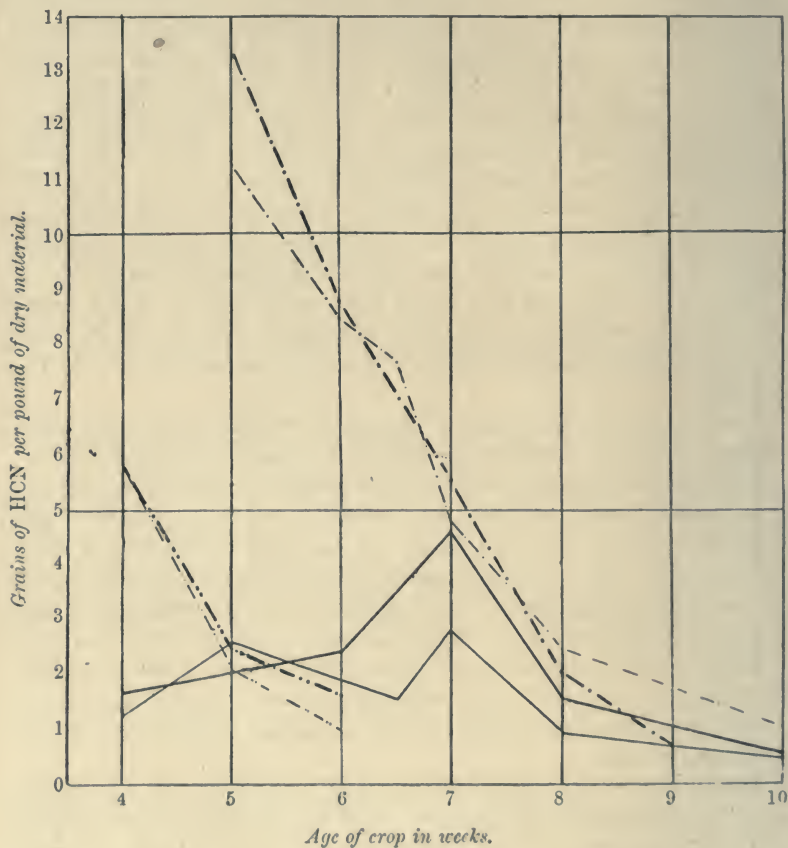
Several samples of sugar cane tops and *paspalum dilatatum*, and couch grass (*cynodon dactylon*) were examined for hydrocyanic acid, but not the slightest trace was found in the macerated samples.

Schönbein-Pagenstecher's test paper gives a ready method of examining fodder plants for glucosides yielding hydrocyanic acid, the sensitiveness of the reaction being greatly increased if the paper is moistened with either formalin solution or alcohol instead of water.

The conclusions drawn from the foregoing results may be summarised as follows :

1. All fodder-plants related to sorghum must be used with discretion, in either the green or dried state, and should not be given in large amounts to animals which have fasted for some time.

2. Sorghums should never be used in a very immature stage of growth, but only when the seed ears are well developed.



----- Planter's Friend, 1st cut, unmanured.  
 - - - - - " " manured.  
 ----- " 2nd cut, unmanured.  
 - - - - - " " manured.  
 ===== Maize, unmanured.  
 ===== " manured.







TABLE III.—*Sorghum*. Variety:—*Early Amber*.

| Date when cut.  | Age in weeks. | Unmanured.            |                  |                           |                | Manured.                    |                |   |                                  |
|---|---------------|-----------------------|------------------|---------------------------|----------------|-----------------------------|----------------|---|----------------------------------|
|   |               | Crops, Lbs. per acre. | Water, Per cent. | Total nitrogen, Per cent. | Ash, Per cent. | Hydrocyanic acid, Per cent. | Ash, Per cent. | Total nitrogen, Per cent.   | Hydrocyanic acid, Grains per lb. |
| First cut or plant crop.                                  |               |                       |                  |                           |                |                             |                |   |                                  |
| 1903. 10/2  | 5             | 610                   | 87.30            | 0.423                     | 2.48           | 0.0108                      | 0.83           | 665   | 0.83                             |
|   |               | 77                    | —                | 3.33                      | 19.52          | 0.085                       | 5.95           | 89  | 5.95                             |
| 25/1  | 6             | 4225                  | 85.50            | 0.367                     | 1.71           | 0.0083                      | 0.58           | 5060  | 0.58                             |
|   |               | 615                   | —                | 2.63                      | 11.79          | 0.067                       | 3.99           | 753   | 3.99                             |
| 2/3   | 7             | —                     | 84.00            | 0.403                     | 1.63           | 0.0056                      | 0.39           | Plants picked, with seed ears not opened out.   |                                  |
|   |               | —                     | —                | 2.62                      | 10.59          | 0.036                       | 2.63           |   |                                  |
| 2/3   | 7             | —                     | 83.00            | 0.417                     | 1.67           | 0.0038                      | 0.27           | Plants picked, with seed ears well opened out.  |                                  |
|   |               | —                     | —                | 2.45                      | 9.83           | 0.022                       | 1.55           |   |                                  |
| 9/3   | 8             | 6020                  | 82.06            | 0.360                     | 1.40           | 0.0030                      | 0.28           | 8530  | 0.28                             |
|   |               | 1187                  | —                | 2.06                      | 7.81           | 0.022                       | 1.53           | 1603  | 1.53                             |
| Second cut or ratoons.                                    |               |                       |                  |                           |                |                             |                |   |                                  |
| 19/3  | 2½            | 1308                  | 89.65            | 0.497                     | 1.43           | 0.0144                      | 1.01           | —   | —                                |
|   |               | 135                   | —                | 4.80                      | 15.74          | 0.159                       | 9.74           | —   | —                                |
| 31/3  | 5             | 979                   | 89.60            | 0.448                     | 1.35           | 0.0100                      | 0.70           | 634   | 0.755                            |
|   |               | 102                   | —                | 4.31                      | 12.98          | 0.036                       | 6.73           | 77  | 6.06                             |
| Kafer corn, grown at the Mackay Sugar Experiment Station. |               |                       |                  |                           |                |                             |                |   |                                  |
| 31/1  | {             | —                     | 76.80            | 0.665                     | 1.73           | 0.0092                      | 0.64           | Plants picked, with seed ears not formed. } Plants were a few days old when analysed. |                                  |
| 31/1  | {             | —                     | 73.50            | 0.413                     | 1.53           | 0.0060                      | 0.42           |   |                                  |
|   | {             | —                     | —                | 1.56                      | 5.78           | 0.023                       | 1.59           | Plants picked, with seed ears opened out. }   |                                  |
| Panicum muticum, grown at Childers.                       |               |                       |                  |                           |                |                             |                |   |                                  |
| 26/3  | {             | —                     | 76.40            | 0.520                     | 2.50           | 0.0045                      | 0.82           | —   | —                                |
|   |               | —                     | —                | 2.24                      | 12.24          | 0.019                       | 1.53           | —   | —                                |
| Panicum maximum, or Guinea grass, grown at Childers.      |               |                       |                  |                           |                |                             |                |   |                                  |
| 26/3  | {             | —                     | 73.05            | 0.686                     | 3.64           | 0.0031                      | 0.21           | —   | —                                |
|   |               | —                     | —                | 2.65                      | 13.97          | 0.012                       | 0.84           | —   | —                                |

TABLE IV.—*Influence of Keeping and Drying on the Amount of Hydrocyanic Acid contained in the Samples.*

|  | Water.<br>Per cent. | HCN.<br>Per cent. | HCN.<br>Grains per lb. |
|--|---------------------|-------------------|------------------------|
| Fresh sample .....   | 85.75               | 0.0117            | 0.82                   |
| Minced sample kept for 38 hours<br>in an open dish (slightly fer-<br>mented) ..... | —                   | 0.082             | 5.74                   |
| “Chaffed” sample kept for 40<br>hours in a canvas bag.....                         | 83.00               | 0.0082            | 0.53                   |
|  | —                   | 0.048             | 3.36                   |
|  | 83.80               | 0.0106            | 0.74                   |
|  | —                   | 0.065             | 4.55                   |
| Fresh sample, ears just formed...  | 86.05               | 0.0041            | 0.28                   |
| Same sample, sun dried and kept<br>for 1 week.....                                 | —                   | 0.029             | 2.03                   |
|  | 10.40               | 0.0242            | 1.69                   |
|  | —                   | 0.027             | 1.80                   |
| Fresh sample, ears well developed  | 74.20               | 0.0028            | 0.20                   |
| Same sample, sun-dried and kept<br>for 1 week.....                                 | —                   | 0.011             | 0.77                   |
|  | 8.75                | 0.0099            | 0.69                   |
|  | —                   | 0.012             | 0.84                   |

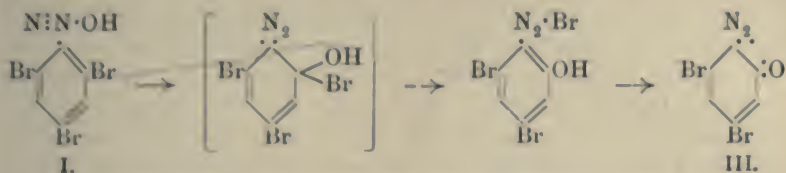
DEPARTMENT OF AGRICULTURE  
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LXXXIII.—*Isomeric Change in Benzene Derivatives. The Conditions Influencing the Interchange of Halogen and Hydroxyl in Benzenediazonium Hydroxides.*

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IN a recent paper (*Proc. Roy. Soc.*, 1903, 71, 153; *Abstr.*, 1903, 84, i, 297) the writer has shown that the *s*-trichloro- and *s*-tribromobenzenediazonium salts of weak acids, such as the acetate, undergo a change in aqueous solution, which results in the replacement of halogen by hydroxyl in an ortho-position in the benzene nucleus with respect to the diazo-group; precisely similar changes occur with even greater readiness in the naphthalene series (*Proc.*, 1902, 18, 252). It was suggested that this change was in all probability due to an isomeric rearrangement of the diazonium hydroxide produced in aqueous solution by hydrolytic dissociation of the salt of the weak acid. The change may be represented in the following manner, in the case of the tribromo-derivative:





The alternative view that the 3:5-dibromo-*o*-quinonediazide\* (diazophenol), III, is the result of the elimination of hydrobromic (or hydrochloric) acid directly from the diazonium hydroxide (I) or from the hydrogen diazotate,  $C_6H_2Br_3 \cdot N:N \cdot OH$ , is improbable.† Elimination of halogen from the benzene nucleus under such conditions is unknown, whereas the mutual interchange of the negative radicle of diazonium salts with the negative groups attached to the benzene nucleus in the ortho- and para-positions relatively to the diazo-radicle is a well-known phenomenon. Thus, Hantzsch and others (*Ber.*, 1896, 29, 947; 1897, 30, 2334; 1898, 31, 1253; and 1900, 33, 505) observed the interchange of chlorine for bromine, and that of both chlorine and bromine for the thiocyno-group; similar rearrangements, in which a nitro-group was replaced by hydroxyl or chlorine, were observed by Meldola and Eyre (*Trans.*, 1901, 79, 1077, and 1902, 81, 988) in the case of the diazotised dinitroanisidines.‡

In the author's previous paper, attention was drawn to the fact that the results, which he obtained, were at variance with those of Hantzsch and Pohl (*Ber.*, 1902, 35, 2964), who state that *s*-tribromobenzenediazonium hydroxide, when present in solutions of the acetate, undergoes a series of transformations, finally yielding *s*-tribromophenylnitrosoamine,  $C_6H_2Br_3 \cdot NH \cdot NO$ . They obtained this substance also from the

\* The author has adopted for the so-called diazophenols the constitution suggested by Wolff (*Annalen*, 1900, 312, 119), who regards this class of compounds as quinonediazides, since true diazoanhydrides, undoubtedly having the linking  $\cdot C:N:N \cdot O \cdot C \cdot$ , are colourless. Recently, Hantzsch (*Ber.*, 1902, 35, 888) has also expressed the opinion that the quinone structure more correctly represents their constitution.

In the former paper, the author used the term "diazoquinone," but this name can only be strictly used for a diazo-derivative of a quinone,  $O:C_6H_3(N_2):O$ , and not for the substances here considered.

† Throughout this paper, the author has used for the salts  $Ar \cdot N:N \cdot OM$  the usual name, "diazotates," and has termed the corresponding acid "hydrogen diazotate"; this acid, which might be called "diazotic acid," has been generally known by the name "diazohydrate." For these compounds, the names "diazoxides" and "diazohydroxides" have recently been suggested (Morgan, *British Association Report*, 1902, p. 191). It is unfortunate that the appropriate terms "diazoate" and "diazoic acid" have been applied to the nitroamines  $\cdot NH \cdot NO_2$  or  $\cdot N:N \cdot NO \cdot OH$ .

‡ Analogous changes have been observed by Gaess and Ammelburg (*Ber.*, 1894, 27, 2211), Meldola and Streatfield (*Trans.*, 1895, 67, 909), and Morgan (*Trans.*, 1902, 81, 1376) in the naphthalene series.

corresponding hydrogen diazotate (diazohydrate), which, according to these authors, changes immediately it is set free from its salts into the nitrosoamine, the hydrogen atom migrating in the following manner:  $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{N} \cdot \text{N} \cdot \text{OH} \rightarrow \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{NH} \cdot \text{NO}$ . A very careful examination has accordingly been made of the transformations undergone both by the diazonium hydroxide and by the hydrogen diazotate; in the course of this investigation, the experiments of Hantzsch and Pohl have been as far as possible exactly repeated.

The author has not been able to demonstrate the formation of a *s*-tribromophenylnitrosoamine. Potassium *s*-tribromobenzenediazotate is quite stable in the presence of excess of alkali; the solution remains colourless even on raising the temperature nearly to the boiling point, no halogen being eliminated. But on reducing the alkalinity either with carbon dioxide or a mineral acid, a yellow colour develops, the characteristic yellow precipitate is formed, and bromine ions appear in the solution.

This yellow precipitate decomposes at  $85^\circ$ , and has the solubilities in various organic media ascribed to the phenylnitrosoamine by Hantzsch and Pohl. The percentage of nitrogen found in the yellow precipitate was 7.6, whereas these authors record 7.67 per cent.; but no estimation of bromine gave a higher value than 63 per cent., whilst they give the values 67.44 and 67.48.

It is further stated that *s*-tribromophenylnitrosoamine hydrochloride is obtained when hydrogen chloride is passed into the ethereal solution of this yellow precipitate. No decomposition point or analysis of the nitrosoamine recovered from the hydrochloride is recorded. When the yellow precipitate obtained by the author was thus treated, the hydrochloride of the 3:5-dibromo-*o*-quinonediazide (III) was alone precipitated; it yielded the diazide (decomposing at  $140^\circ$ ) in an analytically pure state on hydrolysis with water. Moreover, in the original yellow precipitate, small crystals of the quinonediazide are often visible, although covered and matted together with an amorphous condensation product (probably a hydroxyazo-derivative). In addition, the number 539 was found for the molecular weight of the yellow powder determined cryoscopically in benzene solution; if the phenylnitrosoamine has a normal molecular weight in benzene, the value observed should have approximated to the number 359. The amorphous, yellow condensation product left after the quinonediazide is removed from the yellow precipitate (see experimental part) has a molecular weight of more than 900, and therefore contains three benzeneazo-complexes. A mixture of the quinonediazide and the condensation product in certain proportions (about 50 per cent. of each) would have the molecular weight which was actually observed.

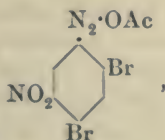
It appears, therefore, that the material described by Hantzsch and

Pohl as "*s*-tribromophenylnitrosoamine," however prepared, is in fact a mixture of a trimolecular condensation product with 3:5-dibromo-*o*-quinonediazide (3:5-dibromo-*o*-diazophenol).

In order to fully define the conditions under which the replacement of halogen by hydroxyl takes place, the influence of other groups, notably the nitro- and the methyl groups, has been studied. The investigation, which has been extended in addition to dihalogendiazo-benzené compounds, has brought out some striking differences. With a nitro-group in the meta-position, as, for example, in 2:4:6-tribromo-3-nitrobenzenediazonium acetate, the exchange of bromine for hydroxyl is very rapid indeed, resembling in this respect the halogen-naphthalene diazonium compounds (Proc., 1902, 18, 252); moreover, in this case a mixture of dibromonitroquinonediazides is formed, not only the ortho-, but also the para-bromine atom being replaced by hydroxyl. From this diazonium compound little, if any, of the condensation product is formed, a fact which supports the view that the latter is a complex hydroxyazo-compound. When a bromine atom is in the meta-position as in 2:3:4:6-tetrabromobenzenediazonium acetate, the isomeric change is also more rapid than in the case of the *s*-trihalogen derivatives.

Most surprising is the fact that 3:5-dibromo-*p*-toluenediazonium acetate does not lose bromine; although the diazonium compound decomposes apparently in the usual manner, no bromine appears in the solution. The influence of the methyl group will be more fully investigated when substituted aromatic monoamines of appropriate constitution are available.

When only two of the positions 2, 4, and 6 are occupied by halogen, very different degrees in the readiness of replacement of halogen by hydroxyl are observed, according as the two halogen atoms are in the positions 2 and 6 with respect to the diazonium radicle, or in the positions 2 and 4. In the former case, bromine is slowly eliminated from the diazonium acetate, but in the latter the change is scarcely appreciable, although there is no doubt that it occurs. If, however, a nitro-group in the meta-position is also present, for example, in 2:4-dibromo-5-nitrobenzenediazonium acetate,



bromine is rapidly eliminated. Although halogen is set free very slowly from 2:4-dichlorobenzenediazonium acetate, a far more rapid



interchange takes place when carbon dioxide is passed into an alkaline solution of the diazotate until it is no longer alkaline to phenolphthalein, but still has this reaction to litmus; about 30 per cent. of the amount of chlorine required for the elimination of one atomic proportion is found as chloride in the solution, a very similar result being obtained when sodium bicarbonate is added to a solution of the hydrogen sulphate.

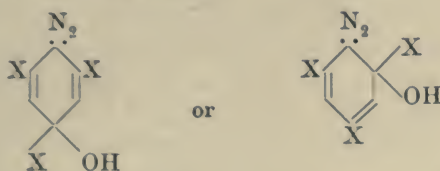
The following list, which shows the percentage of one atomic proportion of halogen eliminated from the diazonium acetate in 20—24 hours at the ordinary temperature, summarises the results obtained with different halogen-benzene and halogen-naphthalene-diazo-compounds. In all cases 3 molecular proportions of sodium acetate were added to one molecular proportion of the diazonium hydrogen sulphate, in order that free mineral acid should be absent from the solution, even if one atomic proportion of bromine was eliminated as hydrogen bromide :

| Diazo-compound.                                 | Percentage of one atomic proportion of halogen set free as chloride or bromide. |
|---|---|
| 2 : 4 : 6-Tribromo-diazobenzene .....           | 64  |
| 2 : 4 : 6-Trichloro-                   ,, ..... | 63  |
| 2 : 4 : 6-Tribromo-3-nitrodiazobenzene .....    | 93  |
| 2 : 3 : 4 : 6-Tetrabromodiazobenzene .....      | 74  |
| 2 : 6-Dibromo-diazobenzene .....                | 24  |
| 2 : 4-Dichloro-                   ,, .....      | trace   |
| 2 : 4-Dibromo-5-nitrodiazobenzene .....         | 80  |
| 1-Chloro-2-diazonaphthalene .....               | 76  |
| 2 : 4-Dibromo-1-diazonaphthalene .....          | 97  |

The results of the experiments described here and in the previous papers, lead to an extension of the views formerly expressed.

These reactions seem in the author's opinion, to be nearly related to the changes which are frequently called "isomeric" or less correctly "intramolecular." Recent experimental evidence as to the mechanism of such changes, is all in favour of the view that most of these transformations either do not take place of themselves or occur only very slowly. The presence of some third substance, the catalyst, the amount of which may in many cases be minute—an idea for which chemistry is indebted to Armstrong—is necessary, at least, to produce an appreciable rate of change. Nevertheless, many instances have been recorded which apparently prove that mere solution in certain solvents—solvents such as alcohol, but not benzene or chloroform—is favourable to (that is, hastens) the change, even when no other substance is present. The interchange of hydroxyl and bromine, considered in this paper, appears to belong to the same

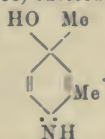
category. The trihalogen-benzenediazonium hydroxide, and the corresponding hydrogen diazotate \* would probably be relatively stable if they could be fixed in the solid state; but when dissolved in water, they are placed under conditions favourable to ionisation and consequently to separation of the complex (diazonium hydroxide, or hydrogen diazotate),  $C_6H_2X_3 \cdot N_2 \cdot OH$ , into the radicles  $(C_6H_2X_3 \cdot N_2) \cdot$  and  $(OH)'$ , which may now reunite in several ways. The original diazonium hydroxide,  $C_6H_2X_3 \cdot N(OH):N$ , or the hydrogen diazotate,  $C_6H_2X_3 \cdot N:N \cdot OH$ , may be regenerated; or, on the other hand, the ortho- or para-quinoid complexes,



may result when the change of the linkings in the complex,  $(C_6H_2X_3 \cdot N_2)$ , involves the benzene nucleus.† If negative groups

\* There is evidence (Hantzsch) that aqueous solutions of the diazonium hydroxides always contain the hydrogen diazotate (diazohydrate). The diazotates exist in two forms, the labile normal or *syn*-diazotate, and the stable *iso*- or *anti*-diazotate. These two forms are, according to Hantzsch, stereoisomeric, and according to Bamberger, structural isomerides. In this paper, only the behaviour of the *isodiazotates* is considered; both the authorities quoted agree in assigning the formula  $Ar \cdot N:N \cdot OM$  to these salts. The existence of the free acid, corresponding with these salts is still doubtful (compare Hantzsch and Pohl, *loc. cit.*), as when set free from its salts, it is transformed into an isomeric neutral substance which is probably the nitrosoamine,  $Ar \cdot NH \cdot NO$ . Compare Hantzsch's "Diazo-Verbindungen" and Morgan's Report to the British Association, 1902, "Our present Knowledge of the Aromatic Diazo-compounds."

† There is a strong and increasing weight of evidence in favour of the view that in isomeric rearrangements of this type the benzene nucleus transiently assumes a quinoid linking. In his recent observations on the changes of *m*-xylylhydroxylamine, in which the hydroxyl group becomes attached to the para-carbon atom, Bamberger (*Ber.*, 1902, 35, 3886) succeeded in isolating the first stage of the trans-



ormation, the  $\psi$ -quinolimine,

Compare also in this connection Lapworth (*Trans.*, 1901, 79, 1265) and Lapworth and Hann (*Trans.*, 1902, 81, 1508), who in their account of desmotropic change have clearly defined the probable changes taking place in the ionised organic complex and have demonstrated their effect on the velocity of the isomeric rearrangement.

Recently, Hantzsch has recorded his opinion that the transformation of diazo-hydrates into nitrosoamines is hastened, if not exclusively brought about, by the ionic dissociation of the former.

occupy the ortho- or para-positions, there is a possibility of these appearing in the solution (as ions), the hydroxyl group remaining attached to the benzene nucleus. If this is the course of the change, the necessary condition for the occurrence of the reaction is the simultaneous presence in the solution of the groups  $(C_6H_2X_3 \cdot N_2)'$  and  $(OH)'$ .

The experimental results fully accord with this view; only the diazonium salts of weak acids change at an appreciable rate, that is, when the diazonium hydroxide formed by hydrolytic dissociation is present in the solution; the more developed the basic character of the diazonium hydroxide, the less readily does the isomeric change proceed; thus 2:4-dichlorobenzenediazonium acetate has scarcely decomposed in this manner after several days, whereas 2:4-dibromo-5-nitrobenzenediazonium acetate rapidly loses bromine. In the presence of alkali (that is, of hydroxyl ions) the diazotates, which form the ions  $(C_6H_2X_3 \cdot N_2 \cdot O)'$  and  $M'$ , are quite stable; only after the hydrogen diazotate,  $C_6H_2X_3 \cdot N_2 \cdot OH$ , is produced by hydrolytic dissociation, on decreasing the concentration of the alkali hydroxide, does the presence of the group  $(C_6H_2X_3 \cdot N_2)$  become possible, and consequently the hydroxyl radicle takes the place of the ortho-bromine atom.

These experiments throw light on another point. The diazo-derivatives of the highly substituted chloro- and bromo-anilines are exceedingly prone to the characteristic diazo-decomposition, in which the atom or group attached to the diazo-radicle takes the place of this group—a decomposition which Hantzsch maintains is peculiar to the *syn*-diazo-compounds. Nevertheless, it has been noted by more than one observer that *s*-tribromophenol cannot be obtained by heating aqueous solutions of *s*-tribromobenzenediazonium salts. On warming an aqueous solution of the hydrogen sulphate of this base, it was observed that a yellow colour developed in a few minutes; after four hours at  $80^\circ$ , the bromide in the solution was estimated, and it was found that 76 per cent. of one atomic proportion of bromine had been eliminated. The presence of the quinonediazide in the yellow liquid was demonstrated by conversion into its hydroxyazo-condensation product with  $\beta$ -naphthol (see experimental part). It is therefore not surprising that *s*-tribromophenol has not been prepared from *s*-tribromobenzenediazonium salts.

Warming of the aqueous solutions of halogenbenzenediazonium salts of mineral acids, in so far as these salts have up to the present been investigated, is always followed by a more or less extensive replacement of halogen by hydroxyl.



## EXPERIMENTAL.

*Replacement of Halogen by Hydroxyl in the case of s-Tribromobenzenediazonium Salts of Weak Acids.*

*Behaviour of the Acetate and Bicarbonate.*—The experiments on the transformation undergone by *s*-tribromobenzenediazonium acetate and bicarbonate, an account of which has previously been given, have been repeated with the object of checking more minutely Hantzsch and Pohl's observations. The copious yellow precipitate, melting and decomposing at 85–90°, which is obtained when a solution of the acetate, whether dilute or concentrated, is kept for 24 hours, was thought by these authors to be *s*-tribromophenylnitrosoamine, but when minutely examined is seen not to be homogeneous, but to consist of long, orange needles covered and matted together with a yellow, amorphous powder. The quinonediazide (diazophenol) can be extracted, not only by shaking the precipitate with water (*loc. cit.*), but also by treating it with hydrogen chloride in ethereal solution in the manner described by Hantzsch and Pohl, when the hydrochloride of the diazophenol (not the nitrosoamine as stated by these authors) separates in nearly colourless needles; these slowly lose hydrogen chloride when kept in a desiccator, and immediately on moistening with water. The diazophenol, when obtained in this manner from the yellow precipitate, crystallises from ether in prisms, melts and decomposes at 140°, the temperature of decomposition depending considerably on the rate of heating; if the substance is slowly heated, it will often decompose at as low a temperature as 132°. A specimen which was prepared by precipitating the hydrochloride from the ethereal solution of the original yellow precipitate, and which should be identical with Hantzsch and Pohl's "*s*-tribromophenylnitrosoamine," gave the following numbers on analysis:

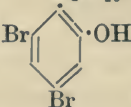
0.124 gave 0.1672 AgBr. Br = 57.4.

$C_6H_2ON_2Br_2$  requires Br = 57.53 per cent.

$C_6H_2Br_3 \cdot NH \cdot NO$  „ Br = 67.96 „

*Coupling of the Quinonediazide with  $\beta$ -Naphthol.*—The quinonediazides (diazophenols) couple very readily with alkaline  $\beta$ -naphthol, giving intensely-coloured solutions. From the *o*-quinonediazides, *o*-dihydroxyazo-compounds are formed, the first examples of which class of substances were recently prepared by Meldola and Eyre (*loc. cit.*). Although both hydroxyl groups are in the ortho-position relatively to the azo-group, these compounds are readily soluble in dilute aqueous alkalis, and yield solutions the colour of which depends on the amount of sodium hydroxide present.

When there is excess of alkali, the colour is deep red, but if the alkali is cautiously neutralised, the solution assumes a very intense magenta or violet; on further addition of acid, the colouring matter is precipitated. This remarkable behaviour constitutes an extremely delicate test for the presence of traces of quinonediazides in aqueous solution. Further, the solubility in aqueous alkalis of their compounds with  $\beta$ -naphthol affords an easy method of separating these dihydroxyazo-derivatives from the ordinary azo- $\beta$ -naphthols, which are insoluble in this solution. In this investigation, this method has been repeatedly employed in order to separate small quantities of quinonediazides from the halogenbenzenediazo-compounds, from which they have been produced by the replacement of halogen by hydroxyl.

3:5-Dibromophenol-2-azo- $\beta$ -naphthol,  $\text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$  , can be

prepared by adding a very dilute aqueous solution of the 3:5-dibromo-o-quinonediazide, obtained by pouring its solution in acetone into a large quantity of water, to an alkaline solution of  $\beta$ -naphthol. The colouring matter is precipitated on acidifying the deep red alkaline solution, and is crystallised from acetic acid containing acetic anhydride, whence it separates in lustrous, copper-coloured plates melting at 214—215°, which, when very small, are red by reflected, and orange by transmitted light:

0.1542 gave 0.1367 AgBr. Br = 37.72.

$\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$  requires Br = 37.91 per cent.

*Properties of the Yellow Amorphous Powder.*—The yellow amorphous powder, which is precipitated together with the quinonediazide, is best prepared by treating an aqueous solution of the diazonium hydrogen sulphate with sodium bicarbonate. To a dilute solution of the sulphate (1 mol.), a 10 per cent. solution of sodium bicarbonate ( $2\frac{1}{2}$  mols.) is slowly added, and the mixture kept for 24 hours, during which period the amount of the precipitate gradually increases. The quinonediazide, which is contained in this precipitate and can be isolated in the manner described above, amounts to 25 per cent. of the yellow solid. In order to obtain the other 75 per cent. of the yellow solid free from the quinonediazide, it is useless to evaporate the ethereal or benzene solution after the separation of the quinonediazide hydrochloride, as only a gum is left. The quinonediazide can, however, be extracted from the yellow precipitate by cold alcohol; during this process, nitrogen is evolved, and it is probable that the amorphous substance is materially changed, as the decomposition point rises, the

longer the treatment with alcohol is continued. The yellow powder thus obtained decomposed at about  $150^{\circ}$ , but prolonged treatment with alcohol raised the temperature of this decomposition to  $185-190^{\circ}$ . The substance is insoluble in alcohol and acetic acid, partially soluble in ether, and completely soluble in cold benzene, from which it is reprecipitated by petroleum. On analysis, it was found to contain 7.5 per cent. of nitrogen, and 61 per cent. of bromine. Cryoscopic determinations of the molecular weight in benzene gave numbers varying from 900 to 920. On attempting to reduce this material with stannous chloride in the presence of acetone, much tar was formed, and a very small quantity of a substance, which appeared to be 3:5-dibromo-*o*-aminophenol, was isolated from the solution; this product melted at  $144^{\circ}$ , and formed an insoluble hydrochloride (compare Bamberger and Kraus, *Vierteljahrsschrift der Naturforsch. Gesell., Zürich*, 1899, 44, 257). All these facts point to the substance being a trimolecular hydroxyazo-condensation product of the quinonediazide, partly with itself, and partly with unchanged *s*-tribromodiazobenzene; but the exact nature of the substance cannot be regarded as settled.

*Exchange of Halogen for Hydroxyl in the Diazonium Nitrites and Cyanides.*—The nitrite and cyanide of *s*-tribromodiazobenzene are of special interest because in certain circumstances, namely, in the presence of cuprous oxide or reduced copper, they both decompose in a characteristic manner, the nitro- or cyano-radicle taking the place of the diazo-group. Further, as Hantzsch has shown that although diazonium cyanides in the solid form exist in rare instances, for example, *p*-anisoldiazonium cyanide, the usual form is a diazocyanide,  $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{CN}$ , which exists in two modifications, a labile *syn*-form, the first product of the action of potassium cyanide on a diazonium salt, and a stable *anti*-form, into which the labile variety more or less readily passes.\* Moreover, Hantzsch has prepared the *syn*-tribromobenzenediazocyanide, and has described it as peculiarly stable.

On mixing dilute aqueous solutions of *s*-tribromobenzenediazonium hydrogen sulphate and potassium cyanide in such proportions that the liquid remained acid in reaction, and then keeping the mixture for four hours at  $10^{\circ}$ , a buff-coloured precipitate rapidly separated, leaving a turbid liquid. This precipitate contained no *s*-tribromophenyl cyanide. Silver nitrate was added after acidifying the filtrate from the solid

\* According to Hantzsch, the *syn*- and *anti*-forms are stereoisomeric,



So far as the author is aware, there are no facts which militate against these substances being structurally isomeric in the sense that in the one compound, the "*syn*," the diazo-group is linked to the nitrogen of the cyano-group,  $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{NC}$ ; in the other, the "*anti*," to the carbon,  $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{CN}$ .



with nitric acid and the precipitate which separated was shown to be silver bromide by estimating the silver in a given weight by reduction in hydrogen. The weight of silver bromide showed that 66 per cent. of one atomic proportion of bromine had been eliminated. The presence of the quinonediazide was demonstrated in the solution by coupling with  $\beta$ -naphthol in the usual manner.

The products of the interaction of *s*-tribromobenzenediazonium hydrogen sulphate and potassium nitrite varied according to the conditions, being more especially dependent on the relative amounts of the two reagents. In all cases, bromine ions appeared in the solution. When a very large excess of potassium nitrite was used (20 mols. to 1 mol.) in extremely dilute solution, the liquid becomes yellow and a nearly white precipitate separates in small amount; 82—86 per cent. of one atomic proportion of bromine appears in the ionic condition; the yellow liquid was shown to contain the quinonediazide. The white solid consisted mainly of 2:4:6-tribromo-1-nitrobenzene, which was obtained in a pure state by distilling the material in steam, and then recrystallising the product from alcohol, whence it separated in colourless prisms melting at 125°. It was identical in all respects with a specimen prepared from 2:4:6-tribromo-3-nitroaniline in the usual manner by eliminating the amino-group (Körner, *Jahresbericht*, 1875, 313).

0.1536 gave 0.239 AgBr. Br = 66.21.

$C_6H_2O_2NBr_3$  requires Br = 66.53 per cent.

So far as the author is aware, the replacement of the diazo- by the nitro-group in the absence of the catalytic accelerating influence of cuprous oxide (Sandmeyer, *Ber.*, 1884, 17, 1633) has not hitherto been observed.

*Replacement of Halogen by Hydroxyl in the case of Alkali  
s-Tribromobenzenediazotates.*

*Preparation of Potassium s-Trihalogenbenzenediazotates.*—Hantzsch and Pohl prepared solid potassium *s*-tribromobenzenediazotates by adding a 5 per cent. solution of the nitrate to 50 per cent. potassium hydroxide. The author has found that this and similar salts can be prepared in well-defined crystals by adding one gram of the diazonium nitrate dissolved in 20 c.c. of water to a solution of 25 grams of potassium hydroxide in 25 c.c. of water at  $-5^\circ$ , and then introducing a cooled solution of 25 grams of potassium hydroxide dissolved in 20 c.c. of water, whereupon the diazotate crystallises out in needles which are fairly stable in air or aqueous solution in the absence of carbon dioxide. As Hantzsch has pointed out, only one form of diazotate

appears to be obtainable from these trihalogenbenzenediazonium salts.

*Potassium s-trichlorobenzenediazotate*, when prepared in this manner, collected on an asbestos filter, and washed with cold alcohol, gave the following numbers on analysis :

0.2315 gave 0.0781  $K_2SO_4$ .  $K = 15.12$ .

$C_6H_2ON_2Cl_3K$  requires  $K = 14.8$  per cent.

In preparing solutions of diazotates, certain precautions are necessary in order to avoid the elimination of halogen ; whenever the resulting solution has a yellow colour, it is a sure indication that halogen has been eliminated and the yellow diazophenol produced. Thus, a 2 per cent. solution of a diazonium hydrogen sulphate cannot be added to an equal volume of 10 per cent. sodium hydroxide with the certainty that no halogen will be eliminated. It is best to use a 1 per cent. solution of the diazonium salt, and half its volume of a 10 per cent. solution of sodium or potassium hydroxide. Bamberger and Kraus (*loc. cit.*) have observed the elimination of halogen when no excess of alkali has been used.

*Coupling of s-Trihalogenbenzenediazo-compounds with Phenols.*—It is obvious from the foregoing that special care has to be exercised in the coupling of this type of diazo-compounds with phenols and naphthols ; for example, Hewitt and Aston (*Trans.*, 1900, 77, 810) found difficulty in preparing a pure hydroxyazo-compound from *s*-tribromobenzenediazonium sulphate and phenol.\* A quantitative yield of the pure hydroxyazo-derivatives can be obtained by the following process. A solution of the diazotate is prepared in the manner just described, and then added to a slight excess of the phenol or naphthol dissolved in the minimum quantity of 10 per cent. solution of sodium hydroxide. As in all probability the coupling takes place between the free hydrogen diazotate formed by hydrolytic dissociation, and the phenol, it is now advisable to reduce the alkalinity ;\* accordingly a 10 per cent. solution of sodium bicarbonate is gradually added in sufficient quantity to nearly convert the whole of the sodium hydroxide into carbonate. In the case of  $\beta$ -naphthol, the whole of the diazo-compound rapidly separates in combination with the naphthol.

\* Goldschmidt (*Ber.*, 1895, 28, 2020) first drew attention to the fact that coupling of a diazotate and a phenol took place between the hydrogen diazotate formed by hydrolytic dissociation and the phenol. The great differences in the readiness with which different diazotates couple is, therefore, to be referred to differences in the degree to which they are hydrolytically dissociated. As is well known, this is one of the great differences between the normal and *iso*-diazotates, the former coupling far more rapidly than the latter, a fact which was pointed out originally by Goldschmidt.

*s*-Tribromobenzenediazo- $\beta$ -naphthol, prepared in this manner, crystallises in lustrous, scarlet needles from glacial acetic acid containing acetic anhydride, and melts at 173—174°; it is insoluble in aqueous 10 per cent. sodium hydroxide, but dissolves readily in alcoholic alkali with a bright red coloration:

0.1316 gave 0.1524 AgBr. Br = 49.3.

$C_{16}H_9ON_2Br_3$  requires Br = 49.49 per cent.

*Effect of Adding a Mineral Acid to an Alkaline Solution of the Diazotate.*—The excess of alkalinity of an alkaline solution of sodium *s*-tribromobenzenediazotate was removed by adding 4 per cent. nitric acid to the liquid, which was cooled to 0° and thoroughly agitated. In order to completely neutralise the mixture, 0.6 per cent. nitric acid was finally used. Following the addition of each drop of nitric acid, a white cloud was formed, which immediately disappeared on shaking the vessel; this white cloud was observed by Hantzsch and Pohl (*loc. cit.*) and thought by them to be the hydrogen diazotate  $C_6H_2Br_3 \cdot N:N \cdot OH$ . As the mixture approached neutrality, the liquid became yellow, and gradually a yellow, amorphous precipitate separated. Finally, the liquid became neutral to litmus and remained neutral during the further addition of a considerable quantity of nitric acid. During this period, the separation of the yellow precipitate rapidly increased: 74 per cent. of one atomic proportion of bromine was found in the ionic condition. The yellow precipitate which, according to Hantzsch and Pohl is *s*-tribromophenylnitrosoamine, decomposed at 85—90°. When treated with ether, a small residue was left undissolved, and from the ethereal solution hydrogen chloride precipitated the hydrochloride of the quinonediazide; the major portion of this substance was dissolved in the large bulk of water used, and could be recognised therein by coupling with  $\beta$ -naphthol.

*Effect of passing Carbon Dioxide into the Alkaline Solution of the Diazotate.*—An alkaline solution of the sodium diazotate was partially neutralised by sodium bicarbonate and then treated with carbon dioxide at 0°. A yellow colour soon appeared, and a yellow precipitate quickly separated. On careful examination, the yellow precipitate was found to consist of small, bright orange needles interspersed among a bulky amorphous solid. This mixture melted and decomposed at 85—90°; hydrogen chloride, when passed into its ethereal solution, caused the hydrochloride of the quinonediazide to separate. In the yellow solution, the quinonediazide could be recognised in the usual manner by means of its  $\beta$ -naphthol derivative. The bromide in the solution represented 82 per cent. of one atomic proportion of bromine. Hantzsch and Pohl state that, in this case also, the yellow precipitate is *s*-tribromophenylnitrosoamine.

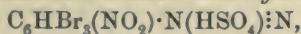


*Action of Sodium Nitrite on s-Trihalogenanilines in Acetic Acid Solution.*—Meldola and Eyre (Trans., 1902, 81, 988) found that on treating dinitro-*p*-anisidine dissolved in acetic acid with sodium nitrite, a nitro-group was displaced by hydroxyl; the *o*-quinonediazide thus formed was isolated as its condensation product with  $\beta$ -naphthol. In order to ascertain the behaviour of the *s*-trihalogenanilines under these conditions, 0.5 gram of *s*-tribromoaniline was suspended in 25 c.c. of glacial acetic acid, and potassium nitrite added in slight excess, whereupon all the solid slowly dissolved. On pouring the solution into 115 c.c. of water, a small amount of a yellow solid separated, which was dissolved in ether and treated therein with hydrogen chloride; the hydrochloride of the dibromoquinonediazide was precipitated in needles, and gave on treatment with water the quinonediazide melting and decomposing at 187°. In the filtrate from the yellow solid, which was also of a yellow colour, the bromide was estimated, 40 per cent. of one atomic proportion of bromine being found.

In a second experiment, the acetic acid solution of the diazotised *s*-tribromoaniline, is poured into a solution of  $\beta$ -naphthol, dissolved in sufficient 10 per cent. solution of sodium hydroxide to insure an alkaline reaction after the addition of the acetic acid. A very dark red precipitate is immediately formed, which consists of a mixture of the sodium salt of the  $\beta$ -naphthol derivative of the quinonediazide and the  $\beta$ -naphthol derivative of *s*-tribromodiazobenzene; a certain amount of the former compound also remains dissolved in the alkali, and can be precipitated by adding acid. The two hydroxyazo-derivatives in the precipitate are best separated by dissolving the mixture in alcoholic sodium hydroxide, care being taken to avoid excess of alkali, which causes the precipitation of the sodium derivatives. The solution is now poured into water, whereupon *s*-tribromobenzenediazo- $\beta$ -naphthol separates, the quinonediazide derivative remaining in solution. The proportion of the hydroxyazo-derivatives was approximately that indicated by the amount of ionic bromine found in the solution.

*Influence of a Radicle in the meta-Position relatively to the Diazo-group on the Replacement of Halogen by Hydroxyl.*

2:4:6-Tribromo-3-nitrobenzenediazonium hydrogen sulphate,



is a singularly insoluble salt; on attempting to prepare it in the ordinary way by adding amyl nitrite to a suspension of the sulphate of the substituted aniline in acetic acid, this salt becomes coated with an insoluble layer of the diazonium hydrogen sulphate and further diazotisation is hindered. The diazonium salt separates in lustrous

needles on adding amyl nitrite to a solution of the substituted aniline in ethyl alcohol containing sulphuric acid, this being the best way of preparing the compound :

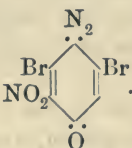
0.2141 gave 0.1021  $\text{BaSO}_4$ .  $\text{SO}_4 = 19.6$ .

$\text{C}_6\text{HO}_2\text{N}_2\text{Br}_3\cdot\text{HSO}_4$  requires  $\text{SO}_4 = 19.8$  per cent.

A solution of this salt in water rapidly became yellow and turbid ; in the presence of sodium acetate, a precipitate which consisted of tufts of microscopic needles, separated in a few minutes ; after two hours, the precipitate was collected and the bromide in the yellow liquid estimated. It represented 93 per cent. of one atomic proportion of bromine, and showed that that proportion of the diazo-compound had been converted into quinonediazide.

*Dibromonitroquinonediazide (dibromonitrodiazophenol),*

$\text{O}:\text{C}_6\text{HBr}_2(\text{NO}_2):\text{N}_2$ ,

probably . The yellow, crystalline solid just mentioned

decomposed at  $138-140^\circ$ , and consisted of a very soluble portion, which, however, rapidly decomposed in alcohol or acetone solution, and an insoluble portion, which decomposed at  $196^\circ$ . On dissolving the mixture in boiling alcohol, lustrous, golden-yellow spangles separated, closely resembling lead iodide, and decomposing at  $196^\circ$ . An estimation of bromine gave numbers showing that the compound was a dibromonitroquinonediazide :

0.1426 gave 0.1654  $\text{AgBr}$ .  $\text{Br} = 49.37$ .

$\text{C}_6\text{HO}_3\text{N}_3\text{Br}_2$  requires  $\text{Br} = 49.51$  per cent.

Its stability indicates that it is a *p*-quinonediazide.

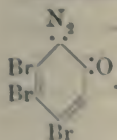
In all probability the soluble unstable portion is the isomeric *o*-quinonediazide. The original yellow mixture gave, on treatment in ethereal solution with hydrogen chloride, a hydrochloride from which water set free a yellow substance decomposing at the same temperature as the original mixture ; the quinonediazide decomposing at  $196^\circ$  yielded a hydrochloride from which it could be regenerated unchanged.

2 : 3 : 4 : 6-*Tetrabromobenzenediazonium hydrogen sulphate,*

$\text{C}_6\text{HBr}_4\cdot\text{N}(\text{HSO}_4):\text{N}$ ,

is readily prepared in the ordinary way from tetrabromoaniline ; it crystallises in needles which are very soluble in acetic acid, methyl alcohol, and water. On adding sodium acetate to its aqueous solution, a crystalline powder separates very rapidly. The amount of bromide found in the solution after four hours shows that 68 per cent. of one atomic proportion of bromine had been eliminated.

*Tribromoquinonediazide* (tribromodiazophenol),  $O:C_6HBr_3:N$ , probably



The yellow, crystalline powder which decomposes at  $120^\circ$  was dissolved in ether and converted into the hydrochloride, from which the quinonediazide was obtained on treatment with water, and decomposed at  $124^\circ$  both before and after recrystallisation from ether.

0.0719 gave 0.1141 AgBr.  $Br = 67.57$ .

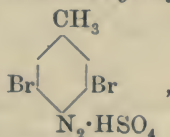
$C_6HON_2Br_3$  requires  $Br = 67.22$  per cent.

Whether this substance is a mixture of the ortho- and para-diazides or the pure ortho-compound, is uncertain; it appeared to be entirely decomposed by boiling alcohol, a fact which indicates that no para-compound is present.

Neither of the foregoing diazonium salts yielded any of the trimolecular condensation product. If the view is correct that this latter material is a hydroxyazo-derivative, its formation would not be possible when the meta-position, relatively to the diazo-group, is occupied by an atom or group other than hydrogen, or when the halogen atom present in the para-position with respect to the diazo-group is replaced by hydroxyl.

*Influence of a Methyl Group in the para-Position Relative to the Diazo-group.*

3:5-Dibromo-*p*-toluenediazonium hydrogen sulphate,



which is extremely easily prepared from 3:5-dibromo-*p*-toluidine by the usual method, crystallises in colourless needles, readily soluble in water, acetic acid, and methyl alcohol, and can be recrystallised by adding ether to its solution in the latter solvent:

0.1542 gave 0.0956  $BaSO_4$ .  $SO_4 = 25.48$ .

$C_7H_5N_2Br_2 \cdot HSO_4$  requires  $SO_4 = 25.66$  per cent.

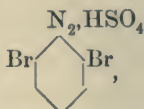
On adding sodium acetate to its aqueous solution, the liquid did not become yellow, but a brown precipitate gradually separated. This product is, however, very unstable, and could not be obtained in a crystalline form. After 20 hours, the filtrate from the copious precipitate was examined for bromide, but no trace could be detected.



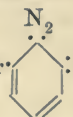
Moreover, on treating the liquid with  $\beta$ -naphthol, none of the colour changes characteristic of the quinonediazides were observed, a small amount of 3:5-dibromo-*p*-tolueneazo- $\beta$ -naphthol alone being formed.

3:5-Dibromo-*p*-tolueneazo- $\beta$ -naphthol.—This latter compound, which can be prepared in the usual manner, crystallises from acetic acid in lustrous, scarlet needles or prisms melting at  $141^{\circ}$ .

*Replacement of Halogen by Hydroxyl in Dihalogenbenzenediazo-compounds.*

2:6-Dibromobenzenediazonium hydrogen sulphate, , is

readily prepared in the usual manner from 2:6-dibromoaniline, and crystallises in needles which are very soluble in acetic acid and methyl alcohol. When treated with sodium acetate in aqueous solution, decomposition appears to take place very slowly; after being kept for 4 days, the yellow solution was filtered from the small quantity of solid, and the bromide estimated in the filtrate which was acidified with nitric acid; the amount showed that 36 per cent. of the diazonium salt had been converted into the quinonediazide. The yellow liquid was extracted two or three times with chloroform and this extract mixed with the chloroform solution of the solid which had separated. Hydrogen chloride was then passed into this solution; the hydrochloride, which separated in white needles, was decomposed with water, thus giving the quinonediazide.

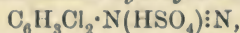
3-Bromo-*o*-quinonediazide, , an orange-coloured powder,

which can be crystallised from ether in prisms, melts and decomposes at  $103^{\circ}$ ; as compared with the other quinonediazides, it is readily soluble in water; its aqueous solution is very sensitive to light, becoming at first brown, and then depositing a brown solid:

0.1340 gave 0.1275 AgBr. Br = 40.49.

$C_6H_3ON_2Br$  requires Br = 40.2 per cent.

2:4-Dichlorobenzenediazonium hydrogen sulphate,



crystallises in very well defined, long, lustrous needles from ethyl alcohol and ether.

2:4-Dichlorobenzeneazo- $\beta$ -naphthol,  $C_{10}H_6(OH) \cdot N_2 \cdot C_6H_3Cl_2$ , was prepared in the manner previously described, by first of all converting the diazonium salt into the diazotate, and then adding the solution

to an alkaline solution of  $\beta$ -naphthol, and subsequently reducing the alkalinity of the mixture with sodium bicarbonate; it crystallises from acetic acid in slender, lustrous, scarlet prisms melting at  $190^{\circ}$ , and is insoluble in aqueous, but soluble in alcoholic, sodium hydroxide:

0.2010 gave 0.1806 AgCl.  $\text{Cl} = 22.23$ .

$\text{C}_{16}\text{H}_{10}\text{ON}_2\text{Cl}_2$  requires  $\text{Cl} = 22.4$  per cent.

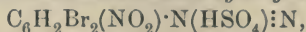
The behaviour of this diazonium salt, when treated with sodium acetate, offers a marked contrast to that of the 2:6-dibromobenzene-diazonium salts. After keeping the solution of the diazonium acetate for 4 days, a faint yellow colour had appeared, and a very small amount of a yellow solid had separated. Moreover, silver nitrate merely gave a turbidity with the solution after acidification with nitric acid. That the yellow colour was due to the formation of quinonediazide was shown by adding the solution to alkaline  $\beta$ -naphthol, when the characteristic magenta coloration developed.

*Treatment of the Dichlorobenzenediazonium Salt with Sodium Bicarbonate.*—On adding aqueous 10 per cent. sodium bicarbonate ( $2\frac{1}{2}$  mols.) to the diazonium sulphate (1 mol.) in a 1.25 per cent. aqueous solution and keeping the mixture for two days, a more extensive change took place. A bulky, yellow precipitate separated from the liquid, which remained throughout acid to litmus. The chloride in the filtrate represented 32 per cent. of one atomic proportion of chlorine. Very little, if any, quinonediazide was contained in the yellow precipitate; what little had escaped condensation with the diazonium salt or with itself, remained in solution. It was recognised therein by adding the filtrate from the yellow precipitate to an alkaline solution of  $\beta$ -naphthol, whereupon 2:4-dichlorobenzeneazo- $\beta$ -naphthol separated, the quinonediazide derivative being left in the alkaline liquor. The latter was precipitated on acidification and purified by redissolving in alcoholic sodium hydroxide and pouring into water; the dichlorobenzeneazonaphthol then deposited was removed and the *chlorophenol-2-azo- $\beta$ -naphthol* precipitated by acid from the magenta-coloured alkaline solution; it formed very dark red flocks, immediately soluble in aqueous alkali hydroxides. The dihydroxyazo-derivative separated from acetic acid in microscopic tufts of needles, melting at  $265^{\circ}$ , but the amount thus obtained was insufficient for analysis.

*Treatment of the Diazotate with Carbon Dioxide.*—Into a solution of the diazotate, prepared in the manner previously described, a rapid current of carbon dioxide was passed, until the solution was no longer alkaline to phenolphthalein, but still had this reaction to litmus. A copious yellow precipitate separated, and after filtration the chloride was estimated in the yellow liquid. It amounted to 34 per

cent. of one atomic proportion of chlorine. As in the previous case, only a very little of the quinonediazide in the form of its azo- $\beta$ -naphthol derivative was isolated.

2 : 4-Dibromo-5-nitrobenzenediazonium hydrogen sulphate,



which crystallises readily, was prepared in order to test the effect of a nitro-group in the meta-position on the transformation of a dihalogendiazonium compound. It was obtained from 2 : 4-dibromo-5-nitroaniline, an account of the method of preparing which will be given on another occasion. On treatment with sodium acetate, its behaviour offered a marked contrast to that of the 2 : 4-dichlorobenzenediazonium compound, a difference which is not due to the fact that one substance has two bromine atoms whilst the other has chlorine, as a comparison of the behaviour of *s*-trichloro- with *s*-tribromo-diazobenzene compounds shows. Transformation began immediately, the solution becoming yellow and a solid being deposited. After 24 hours, the bromine was estimated in the filtered solution; it showed that about 80 per cent. of the diazonium compound had become transformed into the quinonediazide, but much of the latter had condensed; its presence could be demonstrated in the yellow liquid by means of  $\beta$ -naphthol in the usual manner.

The investigation of the type of isomeric change described in this paper is being continued. The author hopes shortly to communicate to the Society the results obtained when different groups or atoms occupy the positions 2, 4, and 6 with respect to the diazo-group.

The author wishes to express his indebtedness to the Chemical Society for the grant from the Research Fund which has defrayed much of the cost of this investigation.

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## LXXXIV.—Freezing Point Curves for some Binary Mixtures of Organic Substances, chiefly Phenols and Amines.

By JAMES CHARLES PHILIP.

### INTRODUCTORY.

It is well known that in general the addition of a small quantity of a substance *A* to another substance *B* lowers the freezing point of the latter, and if the freezing temperatures are plotted against concentra-



tion, a freezing point curve is obtained, starting from the freezing point of *B* and falling towards the concentration axis. The same considerations apply to the effect of small quantities of *B* on the freezing point of *A*, from which also a freezing point curve starts. The initial portions of these curves, where one of the constituents is in large excess, have been very extensively studied with important practical results. But a further interesting field of investigation is opened up by the removal of the restricting condition that one of the constituents should be present in large excess. The problem, which then involves the mutual relationship of the two, so far independent, freezing point curves, and the nature of the solid which separates when freezing takes place in mixtures of widely varying concentration, has been solved in general terms by Roozeboom and Le Chatelier. Providing that the two substances do not form mixed crystals, the complete freezing point curve conforms to one or other of two types according as the substances do or do not form compounds. If no compound is formed, the type of curve is that shown in Fig. 1, where

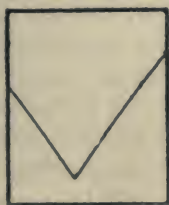


FIG. 1.



FIG. 2a.



FIG. 2b.

the two curves starting from the freezing points of the constituents cut each other at the eutectic point, considerably below the freezing point of either constituent. If a compound is formed, a third curve intervenes (as in Figs. 2a and 2b), which cuts each of the ordinary freezing point curves, and may or may not have a maximum point or summit. If there is a summit, the composition of the mixture, which freezes at this maximum temperature, gives the formula of the compound produced. When the two constituent substances form more than one compound, there is a branch of the composite curve corresponding with each, and when solidification commences in a mixture the composition of which lies within the limits of such a branch, the solid that separates is the compound to which this particular branch belongs.

These types of composite freezing point curves have been experimentally realised for binary systems of various kinds. Thus, curves like that in Fig. 1 have been obtained for mixtures of inorganic salts (Guthrie, *Phil. Mag.*, 1884, 17, 643), for mixtures of metals, such as

cadmium and zinc, tin and zinc, silver and lead (Heycock and Neville, *Trans.*, 1897, 71, 383; *Phil. Trans.*, A, 189, 25), and for mixtures of organic substances, such as acetic acid and benzene, naphthalene and diphenylamine, nitrobenzene and ethylene dibromide (Miolati, *Zeit. physikal. Chem.*, 1892, 9, 649; Dahms, *Wied. Ann.*, 1895, 54, 486; Crompton and Whiteley, *Trans.*, 1895, 67, 327; Roloff, *Zeit. physikal. Chem.*, 1895, 17, 325; Paternò and Ampola, *Gazzetta*, 1897, 27, 481). Examples of the curve type represented in Fig. 2a are supplied for the system salt—water by Roozeboom's classical work on the hydrates of calcium chloride and ferric chloride; for alloys, by Heycock and Neville's work on gold and aluminium (*Phil. Trans.*, A, 194, 201), or Kurnakoff's work on sodium and mercury (see *Abstr.*, 1900, ii, 277); and for organic substances by Kuriloff's work (*Zeit. physikal. Chem.*, 1897, 23, 547, 673), or by the freezing point curves for mixtures of optical isomerides (Roozeboom, *Zeit. physikal. Chem.*, 1899, 28, 505; Adriani, *ibid.*, 1900, 33, 462). Cases where a compound is indicated on the composite freezing point curve by a branch which does not reach a summit occur in freezing point curves for the system salt—water (see Donnan and Burt, this vol., p. 335), and are frequent in the freezing point curves of alloys. Very often a freezing point curve for mixtures of two metals combines the essential features of Fig. 2a and Fig. 2b (see Heycock and Neville, *loc. cit.*, and Kurnakoff, *loc. cit.*).

Apart from Kuriloff's curves, those given for mixtures of optical isomerides, and one or two isolated cases (for example, Schreinemakers, *Zeit. physikal. Chem.*, 29, 581; Lidbury, *ibid.*, 39, 453; van de Stadt, *ibid.*, 41, 353), the freezing point curves hitherto obtained for mixtures of organic substances belong chiefly to the simple type shown in Fig. 1. The work described in the present paper was carried out with the view of obtaining additional examples of mixtures of organic compounds giving curves of the more complex types illustrated by Figs. 2a and 2b.

† Pairs of substances were chosen, chiefly phenols and amines, which might be expected to form compounds, and mixtures of these were made up in different proportions; the fused mixtures were allowed to cool slowly, and the point or points of solidification were determined in each case.

It will be seen from the experimental data given below and from the accompanying diagrams that freezing point curves exhibiting an intermediate branch with a marked summit (as in Fig. 2a) have been found for mixtures of *p*-cresol and aniline, phenol and urea, phenol and *p*-toluidine, phenol and  $\alpha$ -naphthylamine,  $\alpha$ -naphthol and *p*-toluidine, picric acid and phenol. The summit of the intermediate branch of the curve lies generally at 50 molecular per cent.; in one case—phenol and urea—it lies at 33.3 molecular per cent. That is to say,

the compounds, the existence of which is indicated by the form of the freezing point curve, contain in most cases a molecule of each constituent, whilst, in the exceptional case of phenol and urea, 2 molecules of the former combine with one of the latter.

The most interesting case investigated is that of mixtures of phenol and *p*-toluidine, inasmuch as the compound of these two substances exists in two modifications, each of which has a corresponding branch of the freezing point curve, the one enveloping the other.

No case of a freezing point curve exactly of the type shown in Fig. 2*b* has been met with, but a close approximation is furnished by the phenol—urea curve, in which the intermediate branch ends just at the summit, so that one of the eutectic temperatures coincides with the summit temperature.

The extreme slowness with which some of these organic substances crystallise is well illustrated by the behaviour of mixtures of phenol and  $\alpha$ -naphthylamine. Here it is possible to obtain a separation of phenol or  $\alpha$ -naphthylamine in a mixture from which at a considerably higher temperature the compound of these two substances should have crystallised; it is thus possible to realise portions of the primary freezing point curves underneath the intermediate branch.

Contrary to what might have been expected, there is no evidence for the formation of a compound in the case of either phenol and diphenylamine, or *o*-nitrophenol and *p*-toluidine, the freezing point curves for these two systems being of the simple type represented in Fig. 1.

Of the compounds dealt with in the course of the work, the following have not been described: *p*-cresol and aniline, phenol and *p*-toluidine (as plates), picric acid and phenol (1 mol. of each),  $\alpha$ -naphthol and *p*-toluidine.

It should be mentioned that the information given by the freezing point curves has been confirmed and supplemented by analysis of the crystals separating at various points on the curves.

### EXPERIMENTAL.

The method adopted for the determination of the freezing points was essentially that due to Beckmann. Suitable quantities of the two constituents were weighed out in a tube or beaker, surrounded by a larger vessel of the same kind, and the whole was immersed in a bath of appropriate temperature. The fused mixture was allowed to cool, and the commencement of solidification was indicated by surfusion or merely by an alteration in the rate of cooling. Care was taken that the rate of cooling at the freezing point should not be too great, and in most cases excessive surfusion was avoided by introducing the



appropriate solid. As pointed out by previous workers on this subject, the accuracy of the temperature determination cannot be very great, since the temperature observed by the above method is not always the exact freezing point of the mixture under investigation, but is usually a little too low. The error thus introduced will, under similar conditions, be most marked when the composition of the liquid mixture differs widely from that of the crystallising substance.

The composition of the mixtures was either varied by adding fresh quantities of one constituent to the mixture under investigation; or fresh quantities of each constituent were taken for each determination.

The thermometer had a range from 0—100°, and was divided into tenths of a degree; on examination and comparison with a standard thermometer, it was found to give readings which were in general 0.1° too high. In the following tables, the temperatures given are those actually read on this thermometer, for since the object of the investigation was to determine the form of the freezing point curves, the correction of each separately observed freezing point was regarded as superfluous. A second thermometer ranging from -20° to +30° and also divided into tenths, was occasionally used; it was compared with the first thermometer, and its readings were correspondingly reduced.

The materials were redistilled or recrystallised before use, unless a determination of the freezing point had shown them to be sufficiently pure.

#### *Phenol and Diphenylamine.*

The freezing point curve for mixtures of these two substances is of the type shown in Fig. 1; the experimental numbers are given in the following Table I, and the curve itself is shown in Fig. 3. In this curve, as in those to follow, temperature is plotted against molecular percentage.

Of the two freezing points given in the following table (p. 819) for the mixture with 29.3 molecular per cent. of diphenylamine, the higher value, 19.8°, is the point at which phenol begins to crystallise out. As the separation of phenol continues and the temperature accordingly falls, a second freezing point is observed at 18.1°, corresponding with the simultaneous separation of phenol and diphenylamine. The eutectic temperature is therefore 18.1°, and the eutectic mixture contains about 32 molecular per cent. of diphenylamine. This is not far removed from the composition of a mixture containing one molecular proportion of diphenylamine and two of phenol, and indeed the view was at one time held that the eutectic mixture always contains the constituents in simple molecular proportions. This interpretation

TABLE I.

| Weight of phenol. | Weight of diphenylamine. | Percentage of diphenylamine. | Molecular percentage of diphenylamine. | Freezing point. |
|-------------------|--------------------------|------------------------------|--|-----------------|
| 29.08             | 2.44                     | 7.7                          | 4.5                                    | 36.8°           |
| "                 | 5.29                     | 15.4                         | 9.2                                    | 33.3            |
| "                 | 7.91                     | 21.4                         | 13.1                                   | 30.3            |
| 22.28             | 8.35                     | 27.3                         | 17.2                                   | 28.1            |
| "                 | 11.29                    | 33.6                         | 22.0                                   | 24.6            |
| 19.05             | 14.21                    | 42.7                         | 29.3                                   | { 19.8          |
|                   |                          |                              |  | { 18.1          |
| 19.35             | 18.10                    | 48.3                         | 34.2                                   | { [18.5]        |
|                   |                          |                              |  | { 16.2          |
| 16.47             | 22.14                    | 57.3                         | 42.8                                   | 25.0            |
| 13.02             | "                        | 63.0                         | 48.6                                   | 28.3            |
| 9.79              | "                        | 69.3                         | 55.7                                   | 32.0            |
| 7.98              | "                        | 73.5                         | 60.7                                   | 34.4            |
| 9.75              | 33.90                    | 77.7                         | 65.9                                   | 37.1            |
| 6.83              | "                        | 83.2                         | 73.4                                   | 40.4            |
| 4.26              | "                        | 83.8                         | 81.6                                   | 44.1            |
| 1.94              | "                        | 94.6                         | 90.7                                   | 48.2            |
| 0.0               | "                        | 100.0                        | 100.0                                  | 52.6            |

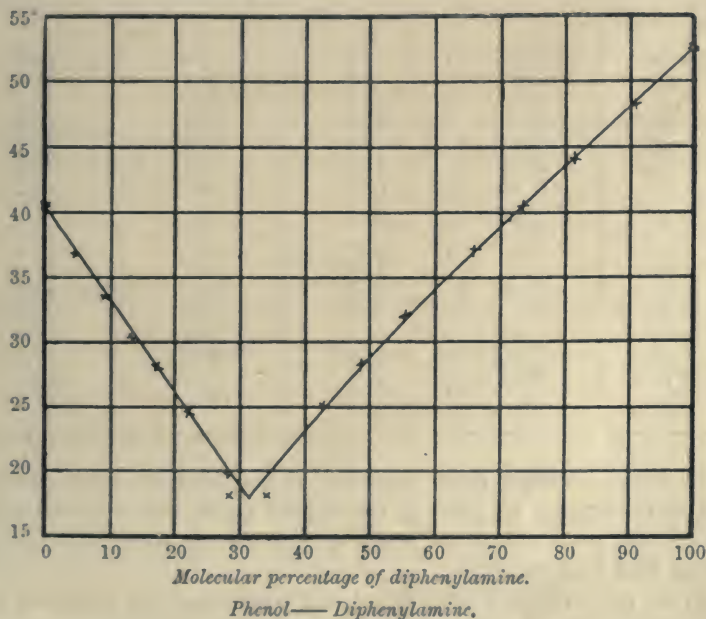


FIG. 3.

of the eutectic mixture has, however, been displaced in favour of the modern view (see Ostwald's *Lehrbuch*, 1, 1023), and the experimental

work of Dahms and others has shown that in the great majority of cases the constituents of the eutectic mixture are not in any exact molecular proportion, the simple ratios obtained in certain cases being probably nothing more than coincidences.

*o*-Nitrophenol and *p*-Toluidine.

In this case, it might have been expected that the freezing point curve would have the form indicated in Fig. 2, owing to the formation of a compound from the two constituents. This combination, however, does not occur, and the freezing point curve consists only of two branches starting from the freezing points of the constituent substances, and melting at a eutectic point, 15.6°, when the molecular percentage of *p*-toluidine is 52 (see Table II and Fig. 4, p. 821).

TABLE II.

| Weight of<br><i>o</i> -nitrophenol. | Weight of<br><i>p</i> -toluidine. | Percentage of<br><i>p</i> -toluidine. | Molecular<br>percentage of<br><i>p</i> -toluidine. | Freezing point. |
|-------------------------------------|-----------------------------------|---------------------------------------|--|-----------------|
| 35.52                               | 0.0                               | 0.0                                   | 0.0  | 44.1°           |
| "                                   | 3.26                              | 8.4                                   | 10.6   | 38.9            |
| "                                   | 6.62                              | 15.7                                  | 19.5   | 34.4            |
| "                                   | 10.38                             | 22.6                                  | 27.5   | 30.2            |
| "                                   | 13.96                             | 28.2                                  | 33.8   | 26.7            |
| 25.92                               | 13.42                             | 34.1                                  | 40.2   | 22.8            |
| "                                   | 17.63                             | 40.5                                  | 46.9   | 18.2            |
| 20.26                               | 17.42                             | 46.2                                  | 52.8   | { 16.1<br>15.6  |
| 18.49                               | "                                 | 48.5                                  | 55.0   | 17.8            |
| 16.60                               | "                                 | 51.2                                  | 57.7   | 20.0            |
| 18.66                               | 27.26                             | 59.4                                  | 65.5   | 24.7            |
| 13.55                               | "                                 | 66.8                                  | 72.3   | 28.9            |
| 10.03                               | "                                 | 73.1                                  | 77.9   | 32.1            |
| 7.40                                | "                                 | 78.6                                  | 82.7   | 34.7            |
| 4.19                                | 30.43                             | 87.9                                  | 90.4   | 38.5            |
| 0.0                                 | "                                 | 100.0                                 | 100.0  | 43.3            |

The double freezing point recorded for the 52.8 per cent. mixture is to be interpreted as before; the higher point was obtained after sowing with *p*-toluidine, the lower steady eutectic point after further sowing with *o*-nitrophenol.

Liquid mixtures of *o*-nitrophenol and *p*-toluidine are deep red, and this fact might be considered to indicate the formation of a compound. The evidence of the freezing point curve, and the examination of the crystals which separate on freezing, however, are both against this view. Thus, yellow crystals of *o*-nitrophenol, melting at about 45°,



separated from the dark red mixture containing 46.9 per cent. of *p*-toluidine.

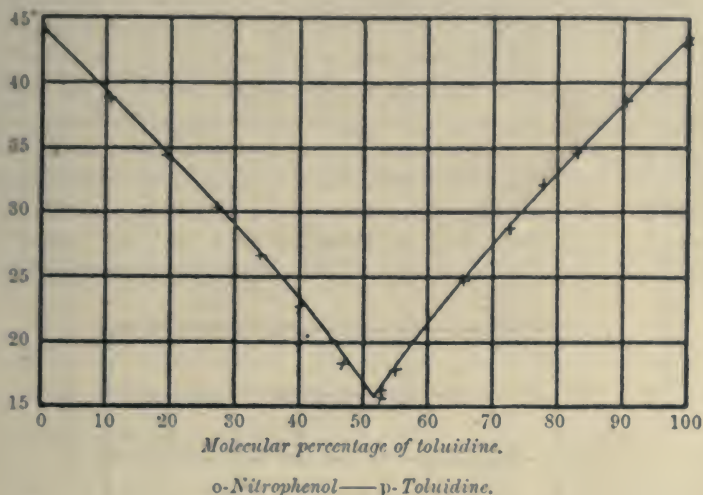


FIG. 4.

*p*-Cresol and Aniline.

The freezing point curve for mixtures containing from 0—67 molecular per cent. of aniline is shown in Fig. 5 p. 822).

TABLE III.

| Weight of <i>p</i> -cresol. | Weight of aniline. | Percentage of aniline. | Molecular percentage of aniline. | Freezing point. |
|-----------------------------|--------------------|------------------------|----------------------------------|-----------------|
| 11.94                       | 0.0                | 0.0                    | 0.0                              | 33.4°           |
| "                           | 1.29               | 9.7                    | 11.1                             | 24.8            |
| "                           | 2.36               | 16.5                   | 18.7                             | 16.8            |
| "                           | 3.86               | 24.4                   | 27.3                             | { 9.4<br>8.7    |
| 8.26                        | 3.35               | 28.8                   | 32.0                             |                 |
| "                           | 5.21               | 38.7                   | 42.3                             | 14.3            |
| "                           | 7.06               | 46.1                   | 49.8                             | 20.0            |
| "                           | 7.23               | 46.7                   | 50.4                             | 21.2            |
| "                           | 7.97               | 49.1                   | 52.8                             | 21.1            |
| "                           | 8.90               | 51.9                   | 55.6                             | 21.0            |
| "                           | 11.09              | 57.3                   | 60.9                             | 20.6            |
| "                           | 14.31              | 63.4                   | 66.8                             | 18.9            |
| "                           |                    |                        |                                  | 15.8            |

A compound is evidently formed in this case, containing a molecular proportion of each constituent, inasmuch as there is an intermediate branch of the freezing point curve with a well-marked summit at 50 molecular per cent. at  $21.2^{\circ}$ . According to theory, the substance separating from any mixture which falls within the limits of the intermediate branch should have a composition defined by the position of the summit. This was borne out in the case of *p*-cresol and aniline by an analysis of the crystals separating from the last mixture, namely, that containing 66.8 per cent. of aniline. The crystals were rapidly filtered at the pump, pressed out on a porous plate, and thus obtained as colourless, scaly plates which were analysed without recrystallisation, the object being to determine the composition of the

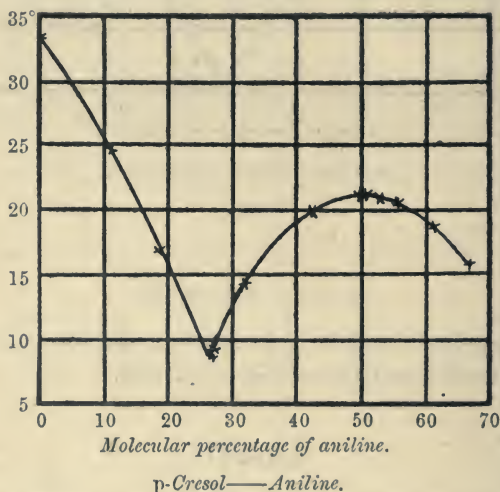


FIG. 5.

crystals as produced under the conditions of experiment. The analysis (by Kjeldahl's method) gave 7.2 per cent. of nitrogen in the crystals, whence the molecular ratio of *p*-cresol to aniline is 1 : 1.06. The high percentage of nitrogen was only to be expected, in view of the way in which the crystals were obtained.

This molecular compound of *p*-cresol and aniline has apparently not been previously prepared.

#### *Phenol and Urea.*

The results obtained with mixtures of phenol and urea containing from 0 to 39.5 molecular per cent. of urea are represented graphically in Fig. 6 (p. 823).

TABLE IV.

| Weight of phenol. | Weight of urea. | Percentage of urea. | Molecular percentage of urea. | Freezing point. |
|-------------------|-----------------|---------------------|-------------------------------|-----------------|
| 11.97             | 0.24            | 2.0                 | 3.0                           | 38.1°           |
| 12.49             | 0.46            | 3.6                 | 5.5                           | { 36.0          |
|                   |                 |                     |                               | { 35.0          |
| 11.94             | 0.65            | 5.2                 | 7.8                           | { 38.0          |
|                   |                 |                     |                               | { 35.1          |
| 10.27             | 0.92            | 8.2                 | 12.3                          | 47.3            |
| 9.43              | 1.63            | 14.7                | 21.3                          | 57.0            |
| 8.91              | 2.07            | 18.8                | 26.7                          | 59.5            |
| 9.48              | 2.89            | 23.4                | 32.3                          | 60.4            |
| 8.63              | 2.87            | 25.0                | 34.3                          | 60.5            |
| 7.58              | 2.66            | 26.0                | 35.5                          | { 62.8          |
|                   |                 |                     |                               | { 60.4          |
| 7.10              | 2.96            | 29.4                | 39.5                          | { 74.5          |
|                   |                 |                     |                               | { 60.0          |

The lowest temperature at which mixtures of phenol and urea can remain liquid is 35°, and the eutectic mixture contains 6.5—7.0 molecular per cent. of urea. The eutectic temperature is given, not only by the point of section of the two branches of the curve, but by the second steady freezing points obtained with the mixtures containing 5.5 and 7.8 molecular per cent. of urea. Further addition of urea causes a rise in the freezing point, the passage of the eutectic point being indicated also by a change in the character of the crystals that separate out. From mixtures containing less than 7 molecular per cent. of urea, a crystallisation of needles takes place, whilst from mixtures containing 7—33 per cent., lustrous plates are produced. At 33 per cent. or thereabouts, the freezing point curve shows a summit, but at this point or just beyond it the curve is cut abruptly by another branch. This passage from one branch of the freezing point

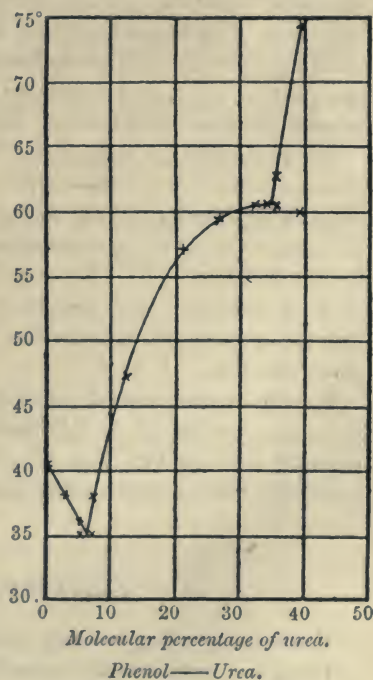


FIG. 6.



curve to another is, moreover, indicated by a change in the nature of the crystallisation, for, instead of plates, a mass of minute crystals is produced when solidification begins.

The freezing points on the steep branch at  $62.8^{\circ}$  and  $74.5^{\circ}$  were very transient; there was no surfusion, and the temperature at which crystallisation began was determined as closely as possible by observation; the reading could be made to within  $0.1-0.2^{\circ}$ , providing that the rate of cooling was slow; the value thus obtained was confirmed by a slight alteration in the rate at which the mixture cooled after the commencement of crystallisation. The second freezing points observed for the mixtures containing 35.5 and 39.5 molecular per cent. of urea were very steady and well-marked; they represent the eutectic point at which the substances corresponding with the branches of the curve crystallise out together.

The summit at 33 molecular per cent. indicates the existence of a compound containing 1 molecule of urea to 2 molecules of phenol, and the plates which crystallise from mixtures containing 7—33 per cent. of urea should consist of this compound. To test this, a mixture was prepared containing 12.2 molecular per cent. of urea; this was completely melted and then allowed to crystallise partially. The separated crystals (plates) were rapidly filtered at the pump, the operation being carried out in a box kept at  $40-50^{\circ}$ , and then pressed out on porous tile previously heated to about  $50^{\circ}$ . The crystals were analysed at once, and found to contain 10.5 per cent. of nitrogen, whence the molecular ratio of urea to phenol is 1:2.2.

The change in the nature of the crystallisation observed on passing the summit at 33 molecular per cent. was confirmed by analysis of the crystals separating from a mixture containing 39.2 molecular per cent. of urea. The filtering apparatus and the drying tile were in this case heated to about  $70^{\circ}$ . The crystals were found to contain 46.6 per cent. of nitrogen, and therefore consisted of urea; hence the steep branch starting at 33 molecular per cent. would end at the freezing point of urea.

The above-mentioned compound of urea and phenol has been described by Eckenroth (*Jahresber.*, 1886, 548); as stated by him, the crystals melt at  $61^{\circ}$ , lose phenol when left exposed to the air, and gradually change into a white powder.

#### *Phenol and $\alpha$ -Naphthylamine.*

The corresponding freezing point curve is shown in Fig. 7 (p. 826).

There is a well-marked summit at 50 molecular per cent. and  $28.8^{\circ}$ ; the eutectic temperatures are  $16.0^{\circ}$  and  $24.0^{\circ}$ , and the eutectic

TABLE V.

| Weight of phenol. | Weight of $\alpha$ -naphthyl-amine. | Percentage of $\alpha$ -naphthyl-amine. | Molecular percentage of $\alpha$ -naphthyl-amine. | Freezing point. |
|-------------------|-------------------------------------|---|---|-----------------|
| 92.25             | 0.00                                | 0.0                                     | 0.0   | 40.4°           |
| 75.88             | 9.55                                | 11.2                                    | 7.6   | 34.2            |
| 58.92             | 20.61                               | 25.9                                    | 18.7  | 21.6            |
| 8.49              | 3.66                                | 30.1                                    | 22.1  | 17.7            |
|                   |                                     |   |   | 16.1            |
|                   |                                     |   |   | 16.8            |
| 7.81              | 3.94                                | 33.5                                    | 24.9  | 15.9            |
|                   |                                     |   |   | 13.2            |
|                   |                                     |   |   | 20.8            |
| 7.54              | 4.77                                | 38.7                                    | 29.4  | 5.5             |
| 6.74              | 5.51                                | 45.0                                    | 35.0  | 24.8            |
| 5.97              | 6.75                                | 53.1                                    | 42.6  | 27.8            |
| 14.41             | 20.18                               | 58.3                                    | 47.9  | 28.6            |
| 13.13             | 20.55                               | 61.0                                    | 50.7  | 28.6            |
| 4.21              | 8.82                                | 67.7                                    | 57.9  | 27.6            |
| 5.05              | 12.05                               | 70.4                                    | 61.0  | 15.9            |
| 3.92              | 10.84                               | 73.4                                    | 64.5  | 25.5            |
|                   |                                     |   |   | 24.0            |
| 9.07              | 26.46                               | 74.5                                    | 65.7  | 21.3            |
| 2.54              | 9.03                                | 78.0                                    | 70.0  | 25.6            |
|                   |                                     |   |   | 24.2            |
| 6.66              | 32.23                               | 82.9                                    | 76.1  | 31.0            |
| 4.26              | "                                   | 88.3                                    | 83.2  | 36.9            |
| 1.32              | 20.14                               | 93.8                                    | 90.9  | 42.5            |
| 0.0               | "                                   | 100.0                                   | 100.0   | 48.3            |

mixtures contain respectively 23.5 and 68 molecular per cent. of  $\alpha$ -naphthylamine.

In this case also, the conclusions drawn from the freezing point curve as to the nature of the substances which crystallise from mixtures of different compositions were confirmed by analysis. The compound of phenol and  $\alpha$ -naphthylamine, the existence of which is proved by the freezing point curve and confirmed by analysis, has been previously prepared by Dyson (Trans., 1883, 43, 469), and its melting point is given by him as 30.1°. The compound is characterised by the extreme slowness with which it crystallises, and owing to this it was possible to realise portions of the first and third branches of the freezing point curve below the eutectic temperatures. Indeed, the intermediate mound could only be realised by adding a small crystal of the compound, which had been already obtained after a few weeks from a mixture containing 32.5 molecular per cent. of  $\alpha$ -naphthylamine. The compound can also be obtained by cooling sufficiently mixtures containing the constituents in approximately molecular proportions. The importance of inoculating the mixture with these crystals will

best be understood by reference to a particular case. When the mixture with 24.9 molecular per cent. of  $\alpha$ -naphthylamine (see table V and figure 7) was cooled in presence of a few crystals of the compound, the freezing point  $16.8^\circ$  was obtained, corresponding with the separation of the compound; after the point  $16.8^\circ$  had been observed, a few small crystals of phenol were added and the cooling continued. After slight surfusion, the thermometer rose to  $15.9^\circ$ , the steady eutectic point. The mixture was now remelted and the liquid cooled to  $12.9^\circ$  in presence of a crystal of phenol alone, after which the

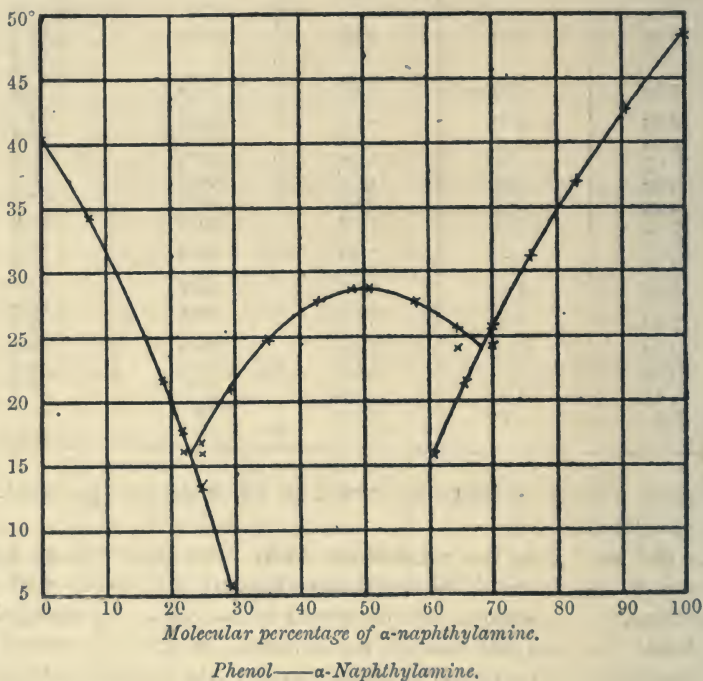


FIG. 7.

temperature rose to  $13.2^\circ$ ; this freezing point lies on the continuation of the curve which starts from the freezing point of phenol, and accordingly the substance separating at  $13.2^\circ$  must be phenol. Another case is recorded in the table where a mixture containing 29.4 molecular per cent. of  $\alpha$ -naphthylamine, for which a freezing point had been found at  $20.8^\circ$ , after inoculation with the compound, was cooled in presence of a crystal of phenol, and then gave a freezing point at  $5.50^\circ$ . Similarly, on the other side of the mound, lower freezing points are found, situated on the continuation of the branch which starts from the



freezing point of  $\alpha$ -naphthylamine. It was hoped that the two branches starting from the freezing points of the constituents might be realised completely as far as their point of intersection, but it was found that phenol or  $\alpha$ -naphthylamine did not separate from mixtures containing approximately molecular proportions of the constituents; when the cooled mixture was inoculated with either substance, it became almost completely solid in a few minutes, owing to separation of the compound.

The sluggishness of the phenol- $\alpha$ -naphthylamine compound is illustrated also by the following experiment. Equal quantities of the liquid mixture containing 64.5 molecular per cent. of  $\alpha$ -naphthylamine were put in each of three watch-glasses, I, II, and III. To I, a little  $\alpha$ -naphthylamine was added, to II a little of the molecular compound, while III was left untouched. Next morning, the contents of III were still liquid; partial crystallisation had taken place both in I and II, but the amount of crystalline matter was obviously greater in II than in I, as might be expected from the freezing points recorded for this mixture. Crystals of  $\alpha$ -naphthylamine and of the compound were now added to III, and by the following morning its contents had shrunk up into a solid mass; this also might have been predicted from the freezing point curve, inasmuch as the eutectic point associated with the simultaneous crystallisation of the two substances is  $24^{\circ}$ , a temperature well above that of the room. It thus appears that when a liquid mixture is supersaturated, firstly and chiefly with regard to the compound, secondly with regard to  $\alpha$ -naphthylamine, the second supersaturation may be removed without disturbing the first (compare Dahms, *loc. cit.*). On the other side of this eutectic point, it was possible to obtain and keep for a limited time liquid mixtures supersaturated firstly and chiefly with regard to  $\alpha$ -naphthylamine, and secondly with regard to the compound, but spontaneous crystallisation of  $\alpha$ -naphthylamine ultimately took place, whilst inoculation with crystals of the compound led to a separation of both substances.

It was not easy, owing to the slow crystallisation of the compound of phenol and  $\alpha$ -naphthylamine, to obtain accurate determinations of the points situated on the mound. Even with very slow cooling after inoculation, there might be considerable surfusion, as, for example, in the case of the mixture with 58 molecular per cent. of  $\alpha$ -naphthylamine. The temperature at the time of inoculation was  $28.35^{\circ}$ , and 40 minutes later it had fallen to  $27.2^{\circ}$ ; a slow rise of temperature then took place, but another 20 minutes elapsed before the crystals were in complete equilibrium with the liquid, and the temperature reached its maximum at  $27.6^{\circ}$ . In other cases, even greater surfusion could not be avoided, and this, obviously, led to

error, all the more when the composition of the liquid differed considerably from that of the substance crystallising out. In some cases, therefore, the freezing point was taken to be the temperature at which the quantity of crystalline matter was obviously increasing; this point was occasionally a few tenths of a degree higher than the maximum temperature subsequently attained.

*Phenol and p-Toluidine.*

For the freezing point data and curve, see Table VI and Fig. 8 respectively:

TABLE VI.

| Weight of phenol. | Weight of <i>p</i> -toluidine. | Percentage of <i>p</i> -toluidine. | Molecular percentage of <i>p</i> -toluidine. | Freezing point. |
|-------------------|--------------------------------|------------------------------------|--|-----------------|
| 30.79             | 0.00                           | 0.0                                | 0.0  | 40.4°           |
| 29.52             | 1.98                           | 6.3                                | 5.6  | 35.5            |
| "                 | 4.35                           | 12.8                               | 11.5   | 29.0            |
| "                 | 6.12                           | 17.2                               | 15.4   | 23.5            |
| 24.29             | 6.44                           | 21.0                               | 18.9   | 18.1            |
| "                 | 7.51                           | 23.6                               | 21.4   | 13.4            |
| "                 | 9.38                           | 27.9                               | 25.3   | 9.5             |
| "                 | 11.40                          | 31.9                               | 29.2   | 15.3            |
| "                 | 13.33                          | 35.4                               | 32.5   | { 20.4          |
|                   |                                |                                    |  | { 19.4          |
| 23.53             | 16.43                          | 41.1                               | 38.0   | { 25.6          |
|                   |                                |                                    |  | { 24.3          |
| 19.84             | "                              | 45.3                               | 42.1   | { 28.0          |
|                   |                                |                                    |  | { 26.5          |
| 16.39             | "                              | 50.0                               | 46.8   | { 29.5          |
|                   |                                |                                    |  | { 28.0          |
| 14.51             | "                              | 53.1                               | 49.8   | { 30.0          |
|                   |                                |                                    |  | { 28.5          |
| 17.20             | 24.25                          | 58.5                               | 55.3   | { 28.8          |
|                   |                                |                                    |  | { 27.5          |
| 14.34             | "                              | 62.8                               | 59.8   | { 27.0          |
|                   |                                |                                    |  | { 26.0          |
| 11.94             | "                              | 67.0                               | 64.1   | { 24.3          |
|                   |                                |                                    |  | { 23.7          |
| 11.31             | 27.32                          | 70.7                               | 68.0   | { 20.6          |
|                   |                                |                                    |  | { 19.7          |
| 10.26             | "                              | 72.7                               | 70.1   | { 20.3          |
|                   |                                |                                    |  | { 19.9          |
| 11.96             | 37.30                          | 75.7                               | 73.3   | 23.9            |
| 8.06              | "                              | 82.3                               | 80.3   | 30.5            |
| 4.69              | "                              | 88.8                               | 87.5   | 35.9            |
| 0.00              | "                              | 100.0                              | 100.0  | 42.8            |

There is a well-marked intermediate branch, the summit of which lies at 28.5° and 50 molecular per cent., this corresponding with the combination of phenol and *p*-toluidine in molecular proportion. The

eutectic temperatures, where the intermediate branch or mound cuts the two ordinary branches, lie at  $8.0^{\circ}$  and  $19.9^{\circ}$ , and the eutectic mixtures contain 24 and 69 molecular per cent. of *p*-toluidine respectively.

The peculiar and interesting feature of the intermediate branch is that it is enveloped by another curve, with a summit at 50 molecular per cent. and  $30^{\circ}$ . The diagram simply expresses the fact that the compound of phenol and *p*-toluidine exists in two modifications, one of which freezes  $1.5^{\circ}$  higher than the other. The evidence for the existence of this double curve will be best appreciated by following

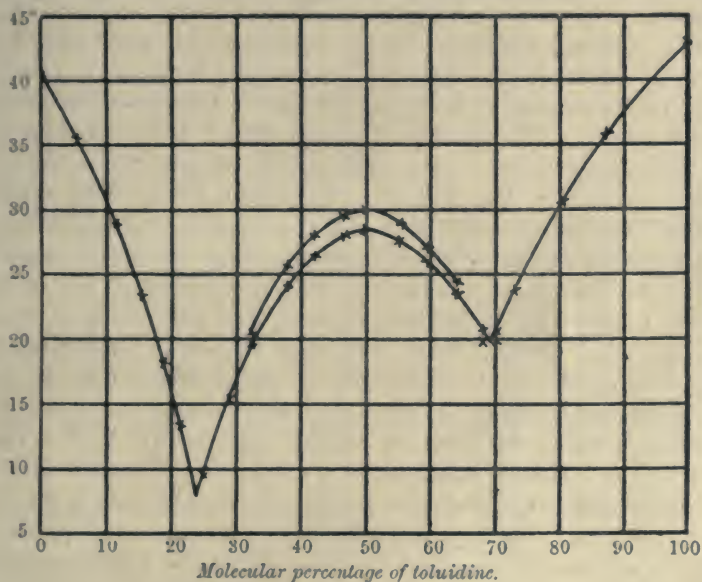


FIG. 8.

the cooling process for a mixture which was found to have two freezing points, as shown in the table and figure. The mixture, for example, containing 49.8 molecular per cent. of toluidine was completely melted and then allowed to cool, when the thermometer readings at intervals of a minute were as follows:  $29.5^{\circ}$ ,  $29.15^{\circ}$ ,  $28.8^{\circ}$ ,  $28.52^{\circ}$ ,  $28.24^{\circ}$ ,  $28.44^{\circ}$ ,  $28.5^{\circ}$ ,  $28.5^{\circ}$ ,  $28.56^{\circ}$ ,  $29.14^{\circ}$ ,  $29.4^{\circ}$ ,  $29.58^{\circ}$ ,  $29.67^{\circ}$ , and so on, gradually up to  $30^{\circ}$ . When this mixture began to crystallise, there was first a separation of glistening plates, and a corresponding slight rise of temperature, as shown above, from  $28.2^{\circ}$  to  $28.5^{\circ}$ . The thermometer halted for a minute or two at this point, but presently



needles made their appearance, the mixture became pasty, and the temperature again began to rise, ultimately reaching  $30^{\circ}$ . These phenomena were regularly observed for all the mixtures represented on the diagram as having two freezing points (except the mixtures with 68.0 and 70.1 molecular per cent. of toluidine, where the lower values are eutectic points). In some cases, the temperature actually fell a little between the first rise and the second.

It has been mentioned that the lower and higher freezing points are apparently associated with the crystallisation of plates and needles respectively. These were obtained in a more definite form by taking a solid mixture of phenol and *p*-toluidine in approximately molecular proportions and crystallising from petroleum ether. Well-formed, lustrous, hexagonal plates separated out, were filtered off and dried on porous tile. After an hour or two, the plates had become opaque, and were converted, at least to a considerable extent, into needle-shaped crystals. The latter product was melted, and on cooling gave two freezing points,  $28.9^{\circ}$  and  $30.5^{\circ}$ , values slightly higher than the summits shown in the diagram. The lower point,  $28.9^{\circ}$ , could be avoided by inoculating the liquid with the acicular crystals and cooling slowly; this is shown by the following readings of the thermometer, taken at intervals of a minute after the addition of the acicular crystals:  $30.72^{\circ}$ ,  $30.6^{\circ}$ ,  $30.5^{\circ}$ ,  $30.4^{\circ}$ ,  $30.3^{\circ}$ ,  $30.2^{\circ}$ ,  $30.14^{\circ}$ ,  $30.1^{\circ}$ ,  $30.05^{\circ}$ ,  $30.02^{\circ}$ ,  $30.12^{\circ}$ ,  $30.23^{\circ}$ ,  $30.31^{\circ}$ ,  $30.37^{\circ}$ ,  $30.45^{\circ}$ ,  $30.5^{\circ}$ . These acicular crystals are evidently the stable form of the compound under the above conditions, and it was in this form that the substance was obtained by Dyson (*loc. cit.*), who gives its melting point as  $31.1^{\circ}$ . The plates have only a transient existence, and are readily converted into the more stable needles. That the plates are formed at all is probably due to the greater rapidity with which they tend to get into equilibrium with the surrounding medium; in other words, the plates crystallise from supersaturated solutions with a greater velocity than the needles. A somewhat similar behaviour is exhibited by potassium nitrate, which, according to a paper just published (Jaffé, *Zeit. physikal. Chem.*, 1903, 43, 575), is often spontaneously deposited from supersaturated solutions in a metastable form. That monotropic substances are met with at all is due to the influence of a similar tendency (compare Ostwald, *Lehrbuch*, 2, [ii], 784).

From the form of the freezing point curve for phenol and *p*-toluidine, it follows that mixtures containing 0—24 molecular per cent. of the base should give crystals of phenol at the commencement of solidification, mixtures with 24—69 molecular per cent. should deposit crystals of the compound, whilst those with 69—100 molecular per cent. should furnish *p*-toluidine. These conclusions were tested by the analysis of the crystals separating from three mixtures containing

respectively 32.8, 66.5, and 70.6 molecular per cent. of *p*-toluidine. The first two mixtures, although differing widely in composition, are both comprised within the limits of the intermediate mound, and in accordance with the foregoing view the crystals separating from them contained respectively 6.5 and 6.9 per cent. of nitrogen (the molecular compound should contain 6.96 per cent.). The crystals separating from the third mixture, which, although differing only slightly in composition from the second, was, however, separated from it by a eutectic point, were found to contain 11.9 per cent. of nitrogen (*p*-toluidine contains 13.1 per cent.). The crystals were separated from the mother liquor simply by filtration and draining on porous tile, recrystallisation not being permissible.

*α-Naphthol and p-Toluidine.*

The corresponding curve is shown in Fig. 9 (p. 832).

TABLE VII.

| Weight of naphthol. | Weight of toluidine. | Percentage of toluidine. | Molecular percentage of toluidine. | Freezing point. |
|---------------------|----------------------|--------------------------|------------------------------------|-----------------|
| 17.01               | 0.00                 | 0.0                      | 0.0                                | 93.9°           |
| "                   | 0.91                 | 5.1                      | 6.7                                | 89.9            |
| "                   | 3.35                 | 16.4                     | 20.9                               | 78.2            |
| "                   | 6.31                 | 27.0                     | 33.3                               | 62.5            |
| 11.40               | 7.05                 | 38.2                     | 45.4                               | 53.1            |
| "                   | 8.69                 | 43.3                     | 50.6                               | 53.6            |
| "                   | 10.86                | 48.8                     | 56.2                               | 52.6            |
| "                   | 13.61                | 54.4                     | 61.6                               | 50.1            |
| 11.30               | 18.38                | 61.9                     | 68.6                               | 44.6            |
| 9.70                | "                    | 65.5                     | 71.8                               | 41.4            |
| 7.01                | "                    | 72.4                     | 77.9                               | { 34.1          |
| 7.87                | 26.51                | 77.1                     | 81.9                               | { 30.3          |
| 5.02                | "                    | 84.1                     | 87.7                               | 30.5            |
| 2.33                | "                    | 91.9                     | 93.9                               | 35.4            |
| 0.00                | "                    | 100.0                    | 100.0                              | 39.7            |
|                     |                      |                          |                                    | 48.1            |

The curve has a summit at 50 molecular per cent. and 53.7°, and thus demonstrates the existence of a compound containing a molecular proportion of each constituent. The eutectic temperatures on either side of the mound are 50.2° and 30.3°, and the eutectic mixtures contain 40 and 81 molecular per cent. of *p*-toluidine respectively. The percentage of nitrogen in the crystals first separating from the mixture containing 68.6 molecular per cent. of toluidine was determined as in the other cases, and found to agree very closely with the value required for the molecular compound.

*Phenol and Picric Acid.*

The freezing point curves for mixtures of picric acid with benzene and with  $\alpha$ - and  $\beta$ -naphthols have been already studied by Kuriloff (*loc. cit.*). According to Gödike (*Ber.*, 1893, 26, 3042), picric acid unites



FIG. 9.

with phenol in the proportion of 1 mol. of phenol to 2 mols. of picric acid, and it seemed interesting to ascertain whether this statement was corroborated by the freezing points, and whether a curve could be obtained with a maximum, not at 50 molecular per cent. as in the



majority of cases hitherto investigated, but at 66 molecular per cent. of picric acid. In the present investigation, phenol and urea had furnished the only case in which the maximum was not situated at 50 molecular per cent.

The freezing point data and curve for mixtures containing 0—74·5 molecular per cent. of picric acid are given in Table VIII. and Fig. 10 (p. 834) respectively.

TABLE VIII.

| Weight of phenol. | Weight of picric acid | Percentage of picric acid. | Molecular percentage of picric acid. | Freezing point. |
|-------------------|-----------------------|----------------------------|--------------------------------------|-----------------|
| 13·04             | 1·41                  | 9·8                        | 4·3                                  | 37·5°           |
| "                 | 2·59                  | 16·6                       | 7·5                                  | 44·2            |
| "                 | 3·89                  | 23·0                       | 10·9                                 | 55·0            |
| 10·63             | 5·36                  | 33·5                       | 17·1                                 | 65·4            |
| "                 | 9·96                  | 48·4                       | 27·8                                 | 75·2            |
| "                 | 11·84                 | 52·7                       | 31·4                                 | 77·5            |
| 6·52              | 9·93                  | 60·4                       | 38·5                                 | 80·9            |
| "                 | 12·11                 | 65·0                       | 43·3                                 | 82·3            |
| 4·82              | 12·32                 | 71·9                       | 51·2                                 | 83·0            |
| 7·05              | 21·83                 | 75·6                       | 56·0                                 | { 81·6          |
| 5·37              | "                     | 80·3                       | 62·5                                 | { 80·6          |
| 4·02              | "                     | 84·5                       | 69·1                                 | 84·2            |
| 3·06              | "                     | 87·7                       | 74·5                                 | 91·8            |
|                   |                       |                            |                                      | 97·4            |

There is a well-marked summit, not, however, at 66 molecular per cent. of picric acid, but with the constituents in molecular proportion, the summit temperature being 83·1°. The eutectic temperatures are 36° and 80·6°, and the eutectic mixtures contain 6 and 58 molecular per cent. of picric acid respectively. According to the curve, crystals of the molecular compound should separate from mixtures containing between 6 and 58 molecular per cent. of picric acid. The bright yellow needles separating from a mixture containing 12·1 molecular per cent. of picric acid were found to contain 12·97 per cent. of nitrogen, whilst the molecular compound should contain 13·0 per cent. Again, the crystals separating from the mixture with 10·9 molecular per cent. of picric acid were found to melt at 84—85°, which practically coincides with the summit of the intermediate branch.

There is therefore no evidence from the freezing point curve in favour of the existence of Gödike's compound (m. p. 53°) of phenol and picric acid, for there is no trace of a summit at 66 molecular per cent. of picric acid. The compound the existence of which is shown by the freezing point curve, and which has been further defined by analysis, contains one molecule of each constituent. The crystals of

this compound lose phenol on exposure, and the point of complete liquefaction of the exposed crystals gradually rises to the melting point of picric acid. An attempt was made to recrystallise the compound from alcohol, but from this solvent well-developed crystals of picric acid were deposited, melting at  $120^{\circ}$ .

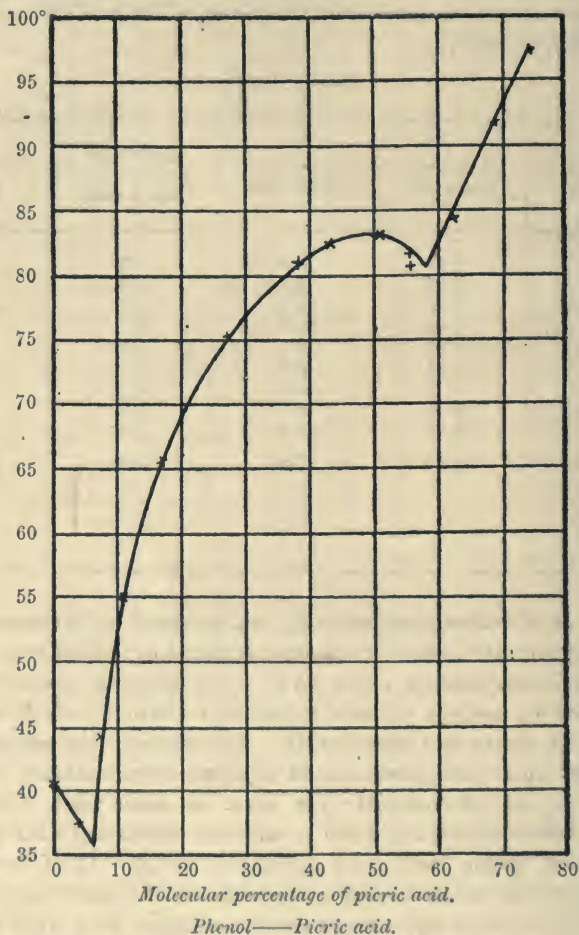


FIG. 10.

The freezing point curves for phenol and picric acid, and also for several of the foregoing mixtures confirm Roozeboom's rule that of the two portions of an intermediate branch on either side of the summit the longer is that which is situated next to the more fusible constituent.

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LXXXV.—*Sulphocamphylic Acid and the Isomeric  $\alpha$ - and  $\beta$ -Camphylic Acids.*

By W. H. PERKIN, jun.

ONE of the most characteristic properties of camphoric acid is the decomposition which this acid undergoes on heating with sulphuric acid when, as Walter first showed (*Ann. Chim. Phys.*, 1843, [iii], 9, 177), it is converted into sulphocamphylic acid according to the equation  $C_{10}H_{16}O_4 + H_2SO_4 = C_9H_{14}SO_5 + CO + 2H_2O$ . Although this sulphonc acid has been known for many years and is so readily prepared, it is remarkable that even at the present time its constitution is not at all understood. A careful examination of its derivatives has proved conclusively that it is a dibasic acid having the formula  $C_8H_{12}(SO_3H) \cdot CO_2H$ , since it yields the dimethyl salt  $C_8H_{12}(SO_3Me) \cdot CO_2Me$  (Koenigs and Meyer, *Ber.*, 1894, 27, 3467) and a sulphochloride,  $C_8H_{12}(SO_2Cl) \cdot CO_2H$  (Perkin, *Trans.*, 1898, 73, 823). A decomposition which is of importance, especially in connection with the present paper, is the behaviour of the crystalline acid ( $C_9H_{14}SO_5 \cdot H_2O$ ) when heated or distilled in superheated steam, when it is decomposed into  $\beta$ -campholytic acid (*isolaunonic acid*) and sulphuric acid,  $C_9H_{14}SO_5 \cdot H_2O = C_8H_{13} \cdot CO_2H + H_2SO_4$ . Furthermore, this reaction is reversible, since sulphocamphylic acid is produced quantitatively when  $\beta$ -campholytic acid is warmed at  $75^\circ$  with sulphuric acid (Perkin, *Trans.*, 1898, 73, 835).

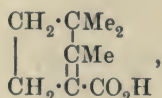
Since  $\beta$ -campholytic acid is inactive and the sulphocamphylic acid obtained from camphoric acid is also inactive, it is exceedingly probable that, in the formation of this sulphonc acid from the strongly dextrorotatory camphoric acid, the first change is the conversion of the latter into  $\beta$ -campholytic acid, which then dissolves in the sulphuric acid, forming sulphocamphylic acid.

This view receives support from the observation, first made by Blanc (*Bull. Soc. chim.*, 1896, [iii], 15, 1191), that camphoric anhydride, when treated with aluminium chloride, is converted into  $\beta$ -campholytic acid with evolution of carbonic oxide,  $C_{10}H_{14}O_3 = C_9H_{14}O_2 + CO$ , a change which is closely allied to that which takes place when camphoric acid is treated with sulphuric acid.

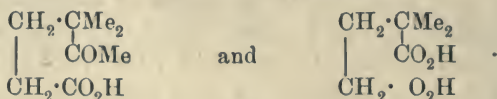
The proof of the close relationship existing between  $\beta$ -campholytic acid and sulphocamphylic acid is of great importance because, if the constitution of the former is established, it should not be a difficult matter to construct a constitutional formula for sulphocamphylic acid.



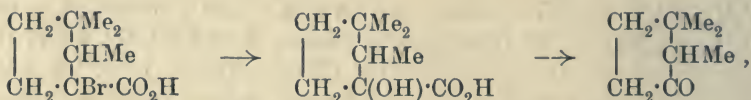
It is now generally supposed that the constitution of  $\beta$ -campholytic acid is represented as follows :



the principal arguments in favour of this formula being the fact that the acid is inactive, and that when oxidised by nitric acid it yields dimethylhexanonic acid and  $\alpha\alpha$ -dimethylglutaric acid :

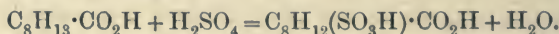


Furthermore,  $\beta$ -camphylic acid combines with hydrogen bromide, and the resulting acid, when treated with baryta, is converted into hydroxy-dihydrocampholytic acid, which is an  $\alpha$ -hydroxy-acid because, on oxidation with lead peroxide, it is converted into the corresponding ketone :



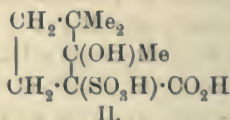
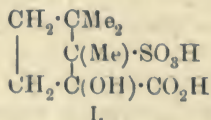
and since this ketone is also formed when the calcium salt of  $\alpha\beta$ -trimethyladipic acid,  $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is distilled, there can be no doubt as to its constitution (Noyes, *Ber.*, 1900, 33, 54; Blaise and Blanc, *Bull. Soc. chim.*, 1902, [iii], 27, 71).

Assuming, then, that the constitution thus assigned to  $\beta$ -campholytic acid is correct, it is important to consider next the nature of the change which takes place when this acid is converted into sulphocamphylic acid according to the equation :



For the sake of convenience, it may be assumed that this change takes place in two stages, the sulphuric acid in the first place combining directly with the  $\beta$ -campholytic acid, and water being then eliminated with formation of sulphocamphylic acid.

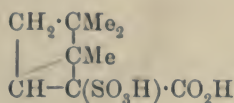
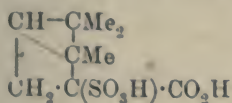
The direct addition of sulphuric acid to the double linking in  $\beta$ -campholytic acid may take place in two different directions and give rise to the two formulæ : \*



\* For a long time, it was assumed that sulphocamphylic acid had the composition  $\text{C}_9\text{H}_{16}\text{SO}_6$ , which would correspond to the above formula, one reason being that the

The difficulty now arising is to distinguish between these two possibilities, and it appears to the author that the consideration of the second stage of the reaction—namely, the elimination of water—supplies a means for doing this.

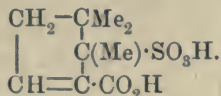
The elimination of water from formula II may take place in two different ways, which may be thus represented :



That the methyl groups cannot take any part in this change is shown by the fact that sulphocamphylic acid, on heating, yields  $\beta$ -campholytic acid, which contains three methyl groups. Apart, then, from the very doubtful possibility of fundamental intramolecular change, the elimination of water can only take place in the ways represented above. But the two formulæ so obtained represent saturated acids, and sulphocamphylic acid is unsaturated, therefore neither of these configurations can be correct, and it is thus proved that formula II cannot represent the product of the addition of sulphuric acid to  $\beta$ -camphylic acid.

The question which at once arises is whether formula I leads to an expression for sulphocamphylic acid which is in accordance with the facts ?

If water is eliminated in the usual way, we obtain the following :

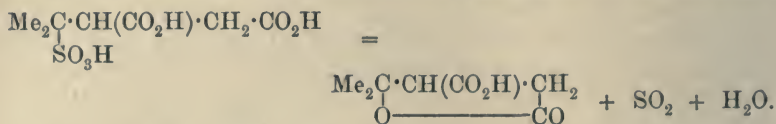


This represents sulphocamphylic acid as an unsaturated acid and explains many of its decompositions, and especially the formation and properties of the camphylic acids described in this paper. On the other hand, one, at least, of the reactions of sulphocamphylic acid is difficult to explain with the aid of this or, indeed, of any other formula derived from  $\beta$ -campholytic acid.

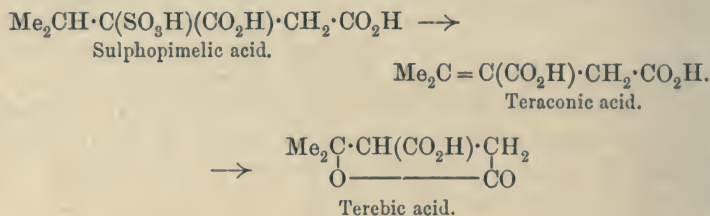
Kachler (*Annalen*, 1873, 169, 181) showed that sulphocamphylic acid, when oxidised by nitric acid, yields sulphopimelic acid and oxalic acid,  $\text{C}_9\text{H}_{14}\text{SO}_5 + 6\text{O} = \text{C}_7\text{H}_{12}\text{SO}_7 + \text{C}_2\text{H}_2\text{O}_4$ .

Koenigs and Hoerlin (*Ber.*, 1893, 26, 2045), in the course of a crystalline acid,  $\text{C}_9\text{H}_{14}\text{SO}_5 \cdot 3\text{H}_2\text{O}$ , on heating, loses two molecules of water much more readily than the third. Since, however, the author has shown (*Trans.*, 1899, 75, 175) that the crystallised acid, when dissolved in water and neutralised with sodium carbonate, is instantly oxidised by permanganate at  $0^\circ$ , it follows that it must exist in aqueous solution as the unsaturated acid,  $\text{C}_9\text{H}_{14}\text{SO}_5$ , and not in the saturated form,  $\text{C}_9\text{H}_{16}\text{SO}_6$ .

careful examination of this sulphopimelic acid, showed that, when heated at 160—170°, it is decomposed with formation of sulphur dioxide and terebic acid, a decomposition which they formulate thus :



It is, however, hardly possible that the sulphonic group in sulphocamphylic acid can be attached to the  $\text{>CMe}_2$  group, because, if this were so, the acid would of necessity be an open chain compound. It appears to the author that the constitution of sulphopimelic acid and its conversion into terebic acid may, more probably, be represented thus :



This view as to the position of the sulphonic group in sulphocamphylic acid is further borne out by the highly important observation of Koenigs and Hoerlin that dimethylmalonic acid,  $\text{Me}_2\text{C}(\text{CO}_2\text{H})_2$ , is also formed when sulphocamphylic acid is oxidised with nitric acid. From this, it follows that the formula of sulphocamphylic acid must contain the grouping  $\text{C}\cdot\text{CMe}_2\cdot\text{C}$ , and it will be noticed that this grouping exists in the formula for this acid suggested on p. 837.

During the course of a long investigation of sulphocamphylic acid on which the author has been engaged for several years, one of the decompositions of this acid which has been most carefully studied is its behaviour on fusion with caustic potash or soda.

Kachler (*Annalen*, 1872, 169, 183), who first investigated this reaction, found that, when fused with caustic potash, sulphocamphylic acid yields a substance,  $\text{C}_9\text{H}_{12}\text{O}_2$ , which melts at 148°. There can be no doubt that this substance is identical with the  $\alpha$ -camphylic acid described in this present paper, and the discovery of this acid is therefore due to Kachler. At a later date, Damsky (*Ber.*, 1887, 20, 2957) repeated Kachler's work, but was unable to isolate the substance melting at 148°. In the place of this, however, he describes the formation of an isomeric acid, which he does not appear to have purified by recrystallisation, and to which he gives the melting point 99°. The author has repeated Damsky's work, and finds that, under the conditions which he employs, the product is always a mixture of the isomeric camphylic acids, and there can therefore be no doubt that



Damsky's product was not a single substance. A part of the results of his investigation of the behaviour of sulphocamphylic acid on fusion with alkali has already been described by the author. In the previous communication (Trans., 1898, 73, 829), it was shown that when sulphocamphylic acid is fused with caustic soda in a cast iron vessel the principal product of the reaction is isolauronic acid ( $\beta$ -campholytic acid).

The explanation of this curious result seems to be that the sodium salts of the camphylic acids are first formed,  $C_8H_{12}(SO_3Na) \cdot CO_2Na + NaOH = C_8H_{11} \cdot CO_2Na + Na_2SO_3 + H_2O$ , and that at  $240^\circ$ , the temperature of the melt, these salts are reduced by the iron of the vessel with formation of the sodium salt of  $\beta$ -campholytic acid,  $C_8H_{11} \cdot CO_2Na + 2H = C_8H_{13} \cdot CO_2Na$ . This reaction will be discussed later in connection with the behaviour of the camphylic acids on reduction (pp. 853 and 868).

The results of the present investigation have also, in some cases, been briefly described in several abstracts in the Proceedings (1892, 55, 68; 1893, 109; 1895, 23; 1896, 189), but a detailed description of the work has always been postponed on account of the difficulty of understanding the constitution of the various substances obtained. Lately, the whole matter has been thoroughly revised, and, although the difficulty of understanding the results is not yet completely removed, it was thought better to publish the work in its present form so that it may be open for discussion.

When sulphocamphylic acid is fused with caustic soda in a nickel basin, the reduction mentioned above is avoided, and the principal product of the reaction is invariably a mixture of  $\alpha$ -camphylic acid (m. p.  $148^\circ$ ) and  $\beta$ -camphylic acid (m. p.  $104^\circ$ ), both of which have the formula  $C_8H_{11} \cdot CO_2H$ . At the same time, small quantities of  $\alpha$ -dicamphylic acid,  $C_{16}H_{22}(CO_2H)_2$  (m. p.  $230^\circ$ ),  $\alpha\alpha$ -dimethylsuccinic acid,  $CO_2H \cdot CMe_2 \cdot CH_2 \cdot CO_2H$ , and other substances are also formed.

The separation of the camphylic acids, which is attended with unusual difficulties, is described in detail in the experimental part of this paper (p. 847).

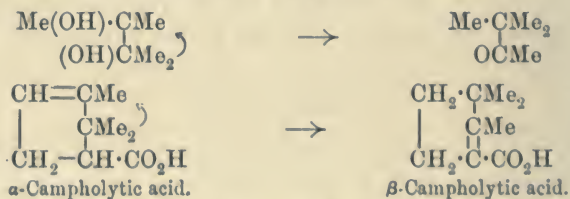
#### *$\alpha$ -Camphylic Acid.*

Taking  $\alpha$ -camphylic acid first, the following is a brief summary of its chief properties. It is a feeble monobasic acid, the ammonium salt of which readily dissociates when its aqueous solution is boiled, but its true acid nature is clearly proved by the preparation of the acid chloride,  $C_8H_{11} \cdot COCl$ , ethyl ester,  $C_8H_{11} \cdot CO_2Et$ , and anilide,  $C_8H_{11} \cdot CO \cdot NH \cdot C_6H_5$ , and therefore the view expressed by Damsky (*loc. cit.*, p. 2965) that Kachler's substance melting at  $148^\circ$ , and which was  $\alpha$ -camphylic acid, did not show the properties of an acid is incorrect.

$\alpha$ -Camphylic acid combines with hydrogen bromide at the ordinary temperature, yielding  *$\alpha$ -camphylic acid dihydrobromide*,  $C_8H_{13}Br_2 \cdot CO_2H$ , a beautifully crystalline substance which melts at  $152^\circ$ , and, when boiled with dilute alkalis, is decomposed into its constituents. When bromine acts on  $\alpha$ -camphylic acid in the dark, addition takes place, and *dibromodihydro- $\alpha$ -camphylic acid*,  $C_8H_{11}Br_2 \cdot CO_2H$  (m. p.  $165-170^\circ$ ), is formed, but in sunlight substitution also takes place and *tribromodihydro- $\alpha$ -camphylic acid*,  $C_8H_{10}Br_3 \cdot CO_2H$  (m. p.  $178^\circ$ ), is produced. When the former substance is digested with acetic acid, hydrogen bromide is eliminated and *monobromo- $\alpha$ -camphylic acid*,  $C_8H_{10}Br \cdot CO_2H$  (m. p.  $107^\circ$ ), is formed.  $\alpha$ -Camphylic acid also exhibits the properties of an unsaturated acid in its behaviour with permanganate, which it instantly reduces, and when oxidised by this reagent at  $0^\circ$  it is converted into an acid,  $C_9H_{14}O_5$  (m. p.  $145^\circ$ ), which is probably a *trihydroxy- $\alpha$ -camphylic acid* having the formula  $C_8H_{10}(OH)_3 \cdot CO_2H$ .

This acid is further oxidised by potassium dichromate and sulphuric acid, yielding a new acid,  $C_6H_{10}O_3$ , a possible constitution for which is given on p. 858.  $\alpha$ -Camphylic acid is reduced by sodium amalgam with difficulty, and is converted into an acid,  $C_8H_{13} \cdot CO_2H$ , which boils at  $162^\circ$  (45 mm.), and the investigation of which clearly proves that it is the *inactive* modification of  *$\alpha$ -campholytic acid*. The  *$\alpha$ -campholytic acid*, which was first obtained by Walker (Trans., 1893, 63, 498) by the electrolysis of the potassium salt of orthoethyl camphorate, is optically active,\* and combines with hydrogen bromide to form bromodihydro- *$\alpha$ -campholytic acid* (m. p.  $98-100^\circ$ ).

It possesses the highly characteristic property that, when digested with dilute sulphuric acid, it is converted into  *$\beta$ -campholytic acid* (*isolaunolic acid*) by a change which is supposed to be due to the wandering of a methyl group, and to be similar to the transformation of pinacone into pinacolone (Lapworth, Report of the Meeting of the British Association, Bradford, 1900, p. 299) :



The reasons for assigning the above formula to  *$\beta$ -campholytic acid* have already been given (p. 836). That the constitution of  *$\alpha$ -campholytic acid* is that represented here was rendered probable by the fact that the acid, on oxidation, yields principally dimethyltricarballic acid :

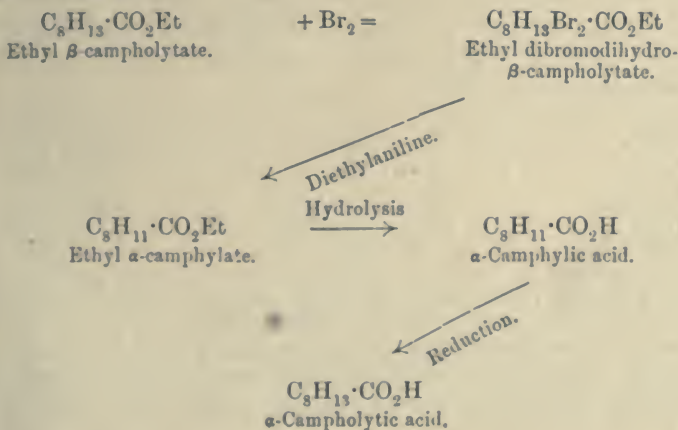
\*  $[\alpha]_D = -5^\circ$ .



The change from  $\alpha$ - to  $\beta$ -camphylic acid is also accompanied by a loss of activity, which is expressed by the fact that the formula of the  $\alpha$ -acid contains an asymmetrical carbon atom, whereas that of the  $\beta$ -acid does not. The inactive acid, obtained from  $\alpha$ -camphylic acid by reduction, possesses all the chemical properties of Walker's  $\alpha$ -campholytic acid, the fact that it is converted into  $\beta$ -campholytic acid on boiling with dilute sulphuric acid being especially noteworthy; it must therefore be regarded as the inactive modification of  $\alpha$ -campholytic acid. This same inactive  $\alpha$ -campholytic acid has recently been prepared synthetically by Perkin and Thorpe (Proc., 1903, 19, 57) by a process which leaves no doubt that the constitution given to this acid above is correct. A point of considerable interest, which has been observed in experimenting on the relationship existing between  $\alpha$ -camphylic acid and  $\beta$ -campholytic acid, is that the former may be obtained from the latter, not only through the intermediate step (sulphocamphylic acid), but also in the following way.

When ethyl  $\beta$ -campholytate,  $\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{Et}$ , is treated with bromine, it is converted by addition into ethyl dibromodihydro- $\beta$ -campholytate,  $\text{C}_8\text{H}_{13}\text{Br}_2\cdot\text{CO}_2\text{Et}$ . If this dibromo-ester is digested with diethylaniline, it loses 2 molecules of hydrogen bromide, and an ester,  $\text{C}_8\text{H}_{11}\cdot\text{CO}_2\text{Et}$ , is formed, which is ethyl  $\alpha$ -camphylate, since, on hydrolysis, it yields  $\alpha$ -camphylic acid melting at  $148^\circ$ .

This result not only shows the close relationship existing between  $\alpha$ -camphylic acid and  $\beta$ -campholytic acid, but it also affords a means of converting  $\beta$ -campholytic acid into  $\alpha$ -campholytic acid, as is shown by the following scheme:



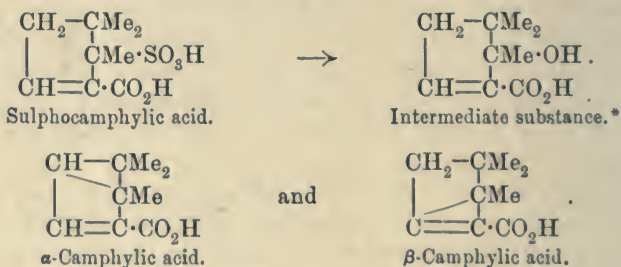


It was mentioned on p. 840 that  $\alpha$ -campholytic acid, when boiled with dilute sulphuric acid, is converted into  $\beta$ -campholytic acid, the change being accompanied by the wandering of a methyl group.

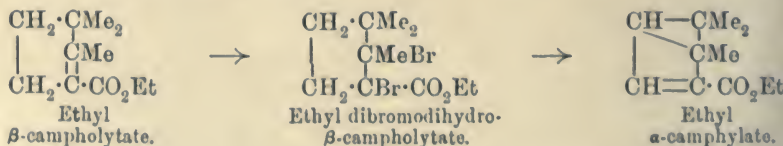
Since  $\beta$ -campholytic acid can be converted into  $\alpha$ -campholytic acid by the above scheme, it appears that the methyl group is also able to wander in the reverse direction, the two changes being, in fact, very similar to an ordinary case of tautomerism. It is because of the occurrence of intramolecular changes such as these that it has been found so difficult to determine with certainty the constitution, not only of the acids described in the present paper, but also of other substances belonging to the camphor group.

### *The Constitution of $\alpha$ -Camphylic Acid.*

Two methods of formation of  $\alpha$ -camphylic acid are known, both of which confirm the same view as to the constitution of this acid. The first of these is the conversion of sulphocamphylic acid into the  $\alpha$ - and  $\beta$ -camphylic acids by fusion with caustic soda, a decomposition which, in the author's opinion, may be expressed in the following way :



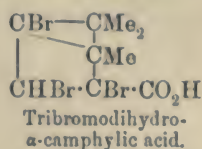
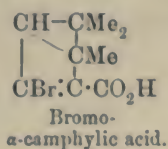
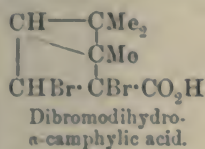
The second method of formation of  $\alpha$ -camphylic acid is the conversion of ethyl  $\beta$ -campholytate into ethyl dibromodihydro- $\beta$ -campholytate and subsequent removal of two molecules of hydrogen bromide by boiling with diethylaniline (p. 861).



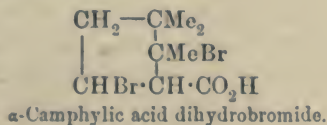
\* It is interesting to note that a considerable quantity of water is always given off when the dry product of the fusion of sulphocamphylic acid is distilled. This behaviour seems to indicate that the product obtained on acidifying the melt consists largely of this intermediate hydroxydihydrocamphylic acid which, then, during the subsequent distillation, decomposes with elimination of water and formation of the  $\alpha$ - and  $\beta$ -camphylic acids.

The formation of trimethylene derivatives in this way is not remarkable, as several cases very similar to the above have been observed during recent years, especially in the terpene series.

$\alpha$  Camphylic acid, indeed, behaves as though it were unsaturated and, at the same time, a trimethylene derivative; thus bromine adds itself to the double linking, but, as is so frequently the case, leaves the trimethylene ring untouched. The constitution of *dibromodihydro- $\alpha$ -camphylic acid* and of the other derivatives obtained by the action of bromine and mentioned on p. 851 may therefore be thus represented:

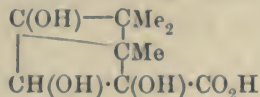


On the other hand,  $\alpha$ -camphylic acid combines with two molecules of hydrogen bromide, both the double linking and the trimethylene ring taking part in the change and the constitution of the product thus formed is therefore probably as follows:

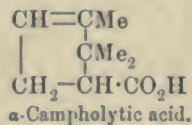
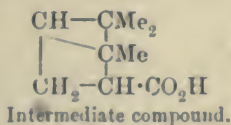
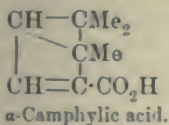


although the positions occupied by the bromine atoms have not, as yet been proved.

On oxidation,  $\alpha$ -camphylic acid is converted into a monobasic acid,  $\text{C}_9\text{H}_{14}\text{O}_5$  (p. 855), which does not combine with hydroxylamine and which, since it has all the properties of a polybasic hydroxy-acid, is probably a *trihydroxydihydro- $\alpha$ -camphylic acid* having the formula



Lastly, the formation of  *$\alpha$ -campholytic acid* from  $\alpha$ -camphylic acid by reduction, in boiling alkaline solution, with excess of sodium amalgam, may be represented thus:



Such a change is, of course, remarkable, but this tendency of a trimethylene ring compound, under certain conditions, to undergo intramolecular change into the corresponding unsaturated compound has

been observed before. Thus, for example, carone, when heated, is converted into  $\Delta^3$ -*p*-menthenone :

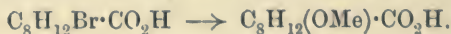


It will be noticed that, if such a change is assumed to take place in the case of the intermediate compound shown above, a methyl group must wander in order to equalise the valencies.

### *β-Camphylic Acid.*

In order to be able to discuss the constitution of this acid, the following summary of its principal properties and of the derivatives which have been obtained from it may be given.

*β*-Camphylic acid,  $\text{C}_8\text{H}_{11}\cdot\text{CO}_2\text{H}$ , differs sharply in some of its reactions from the isomeric *α*-acid ; thus, for example, it is not reduced, even on boiling in alkaline solution, with a large excess of sodium amalgam.\* Again, when treated with hydrobromic acid, it takes up only one molecule of hydrogen bromide, yielding *isobromodihydro-β-camphylic acid*,  $\text{C}_8\text{H}_{12}\text{Br}\cdot\text{CO}_2\text{H}$  (m. p.  $138^\circ$ ), whereas *α*-camphylic acid, under exactly similar conditions, combines with two molecules of hydrogen bromide. This *isobromodihydro*-acid of melting point  $138^\circ$  is isomeric with the *bromodihydro-β-camphylic acid* which had previously been obtained (Perkin, *Trans.*, 1898, 73, 827) from sulphocamphylic bromide by the action of heat,  $\text{C}_8\text{H}_{12}(\text{SO}_2\text{Br})\cdot\text{CO}_2\text{H} = \text{C}_8\text{H}_{12}\text{Br}\cdot\text{CO}_2\text{H} + \text{SO}_2$ , and which melts at  $128\text{--}129^\circ$ . The latter of these isomeric acids, when treated with alcoholic potash, is decomposed into hydrogen bromide and *β*-camphylic acid. A different behaviour is shown by the *isobromo*-acid which melts at  $138^\circ$ , since, when digested with methyl-alcoholic potash, it does not yield *β*-camphylic acid, but is converted, almost quantitatively, into *methoxydihydro-β-camphylic acid* (m. p.  $94^\circ$ ).



\* In one of the preliminary notices on sulphocamphylic acid (*Proc.*, 1896, 190), it was stated that *β*-camphylic acid, when treated with sodium amalgam, yields an acid melting at  $130^\circ$  which was named *iso-β-camphylic acid* and the acid-chloride, ethyl salt, and anilide of which were described, as also the products obtained by oxidising it with permanganate. Subsequent investigation has shown that this acid was in reality *β*-campholytic acid. Probably the specimen of *β*-camphylic acid used in these experiments had been prepared by fusing sulphocamphylic acid with caustic potash or soda in a cast iron vessel and was therefore contaminated with *β*-campholytic acid, the remarkable formation of which, by the reducing action of the iron of the vessel, was then not understood.

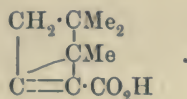


In its behaviour with bromine,  $\beta$ -camphylic acid shows the closest similarity to the  $\alpha$ -acid. It is readily acted on by bromine with formation of *dibromodihydro- $\beta$ -camphylic acid*,  $C_8H_{11}Br_2 \cdot CO_2H$  (m. p.  $172^\circ$ ), and this, when boiled with glacial acetic acid, or treated with alcoholic potash, is converted, by the loss of one molecule of hydrogen bromide, into *bromo- $\gamma$ -camphylic acid*,  $C_8H_{10}Br \cdot CO_2H$  (m. p.  $148-152^\circ$ ).

$\beta$ -Camphylic acid is readily oxidised by permanganate, and when the operation is carried out at  $0^\circ$  it is converted, apparently quantitatively, into a syrupy acid which, on analysis, gives numbers agreeing with the formula  $C_9H_{14}O_5$ . Since this acid reacts both with phenylhydrazine and with acetyl chloride, it is probably a *keto-dihydroxydihydro- $\beta$ -camphylic acid*,  $C_7H_{11}(OH)_2(CO) \cdot CO_2H$ . The most important point in connection with this acid is that, on further oxidation with potassium dichromate, it yields  *$\alpha\alpha$ -dimethylsuccinic acid*,  $CO_2H \cdot CMe_2 \cdot CH_2 \cdot CO_2H$ .

#### *Constitution of $\beta$ -Camphylic Acid.*

In discussing the formation of the  $\alpha$ - and  $\beta$ -camphylic acids from sulphocamphylic acid by fusion with caustic soda, two possible formulæ were given for these acids, and the following was selected to represent  *$\beta$ -camphylic acid* (p. 842):



With the aid of this expression the formation of the syrupy acid,  $C_9H_{14}O_5$ , by oxidation with permanganate and the subsequent further oxidation of this acid to dimethylsuccinic acid are readily understood and may be formulated thus:



Ketodihydroxydihydro- $\beta$ -camphylic acid.

$\alpha\alpha$ -Dimethylsuccinic acid.

It is obvious that an acid having the constitution assigned to  $\alpha$ -camphylic acid on p. 842 could not yield  $\alpha\alpha$ -dimethylsuccinic acid on oxidation.

Again, the other chief points of difference between  $\alpha$ - and  $\beta$ -camphylic acids can be satisfactorily explained if the two formulæ on p. 842 are accepted as representing these two acids.

Thus,  $\alpha$ -camphylic acid combines with two molecules of hydrogen bromide, both the double linking and the trimethylene ring taking part in this reaction (p. 843), whereas  $\beta$ -camphylic acid combines with

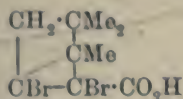
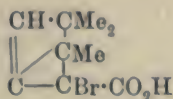
only one molecule of hydrogen bromide, the trimethylene ring remaining intact. The trimethylene ring varies very much in stability according to the groups attached to it, but a ring of the kind represented in the formula of  $\alpha$ -camphylic acid is always readily resolved by the action of hydrogen bromide. Thus, for example, carone is readily acted on by hydrogen bromide with the formation of 8-bromo-menthanone:



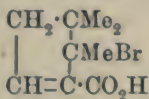
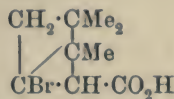
On the other hand, the three-carbon or *cyclopropene* ring contained in the formula of  $\beta$ -camphylic acid is of quite a different nature, and might therefore be expected to show great differences in stability from the trimethylene ring in  $\alpha$ -camphylic acid. Very few *cyclopropene* derivatives have so far been prepared, but among these the *methylcyclopropenedicarboxylic acid*,  $\text{MeCH} \begin{array}{c} \diagup \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{array}$  discovered by Feist (*Ber.*, 1893, 26, 750) may be mentioned because it contains a three-carbon grouping similar to that contained in the above formula of  $\beta$ -camphylic acid.

Like the latter acid, *methylcyclopropenedicarboxylic acid* combines with two atoms of bromine, yielding dibromomethyltrimethylenedicarboxylic acid,  $\text{MeCH} \begin{array}{c} \diagup \text{CBr} \cdot \text{CO}_2\text{H} \\ | \\ \text{CBr} \cdot \text{CO}_2\text{H} \end{array}$ , and from preliminary experiments carried out by the author it appears to combine with only one molecule of hydrogen bromide. Most interesting is the observation of Feist, that it is not reduced by sodium amalgam or even by treatment with sodium in boiling *isoamyl*-alcoholic solution. It will be remembered that one of the most remarkable differences between the  $\alpha$ - and  $\beta$ -camphylic acids is the fact that the former, unlike the latter, is reduced by boiling with sodium amalgam in alkaline solution. This difference finds its explanation in the assumption that  $\beta$ -camphylic acid contains the *cyclopentene* ring which, apparently, resists reduction in a remarkable way. The other derivatives of  $\beta$ -camphylic acid mentioned in this paper may be easily formulated with the aid of the above expression for the constitution of this acid. Thus  $\beta$ -camphylic acid readily combines with bromine, and the resulting dibromide and the bromo- $\gamma$ -camphylic acid\* obtained from it by the elimination of hydrogen bromide may be represented thus:

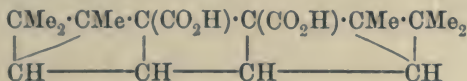
\* This bromo-acid is derived from a third or  $\gamma$ -modification of camphylic acid which has not yet been prepared.

Dibromodihydro- $\beta$ -camphylic acid.Bromo- $\gamma$ -camphylic acid.

$\beta$ -Camphylic acid combines with hydrogen bromide, yielding *iso*-bromodihydro- $\beta$ -camphylic acid, and the isomerism existing between this substance and the bromo-acid, which is obtained by the action of heat on sulphocamphylic bromide (Trans., 1898, 73, 827), is readily explained with the aid of the formulæ :

Bromodihydro- $\beta$ -camphylic acid.*iso*Bromodihydro- $\beta$ -camphylic acid.

When sulphocamphylic acid is fused with soda, varying quantities of a saturated dibasic acid,  $\text{C}_{16}\text{H}_{22}(\text{CO}_2\text{H})_2$ , are formed ; this melts at about  $230^\circ$ , and is described in detail in the experimental part of this paper (p. 862). Since this acid, on distillation, is converted into  $\alpha$ -camphylic acid, it is evidently a dimolecular polymeride of this latter acid, and probably has the formula



This acid has therefore been named  $\alpha$ -dicamphylic acid, and its relationship to  $\alpha$ -camphylic acid is evidently of the same kind as that which exists between the truxillic acids and cinnamic acid.

#### *Preparation and Separation of the Camphylic Acids.*

In preparing these acids, sulphocamphylic acid (50 grams) is dissolved in strong caustic soda solution (containing 150 grams of NaOH) and the solution concentrated in a nickel basin, the residue being maintained at a temperature of about  $210^\circ$  until frothing ceases.

The fused product, which is grey in colour, is dissolved in hot water, cooled, acidified with hydrochloric acid, and the resinous precipitate extracted three times with ether. The ethereal solution, after drying over calcium chloride, is evaporated to a small bulk and allowed to stand, when generally, but not always, crystals of  $\alpha$ -dicamphylic acid (p. 862) slowly separate. After some days, the crystals are collected, the ethereal solution evaporated, and the green residue distilled under reduced pressure, when almost the whole quantity passes over at



190—200° (120 mm.) as a pale green oil which on cooling solidifies almost entirely. The mass is dissolved in dilute aqueous sodium carbonate, the solution filtered from a small quantity of an insoluble oil, boiled with animal charcoal, filtered, and precipitated with hydrochloric acid. After collecting at the pump and washing with water, the residue, which is now only slightly coloured, is recrystallised from 60 per cent. acetic acid, when a colourless, crystalline cake is obtained which consists of a mixture of  $\alpha$ - and  $\beta$ -camphylic acids.

In order to separate these isomerides, the whole is dissolved in dilute ammonia and *slowly* distilled in steam, when the ammonium salt of  $\alpha$ -camphylic acid dissociates more readily than that of the  $\beta$ -acid.

The distillate, on acidifying, yields a white, crystalline precipitate, and the contents of the distilling flask, on cooling, deposit a brown, crystalline mass. These are mixed, dissolved in ammonia, and again distilled in steam, when, if the operation has been properly carried out, crystals separate in the flask at the boiling temperature which are identical with those obtained on acidifying the distillate, and consist of almost pure  $\alpha$ -camphylic acid (m. p. 148°).

After the solution of the ammonium salt has been distilled in steam until no more  $\alpha$ -camphylic acid separates, it yields, on acidifying, crude  $\beta$ -camphylic acid (see p. 866). By recrystallising the intermediate fractions and constantly repeating the ammonia treatment, it is possible to almost completely separate the  $\alpha$ - and  $\beta$ -camphylic acids, but the process is an exceedingly tedious one.

It is stated above that when the crude product of the action of fused caustic soda on sulphocamphylic acid is fractionated almost the whole quantity distils at 190—200° (120 mm.); there is, however, always a small fraction boiling below this temperature. This was collected from a number of fusions and carefully fractionated, when an oil was obtained which distilled at 225—230° under the ordinary pressure, and, on examination, was found to consist of the *anhydride* of *as-dimethylsuccinic acid*:

0.1102 gave 0.2278 CO<sub>2</sub> and 0.0643 H<sub>2</sub>O. C = 56.4; H = 6.5.

C<sub>6</sub>H<sub>8</sub>O<sub>3</sub> requires C = 56.3; H = 6.2 per cent.

This oil was insoluble in cold alkalis, but dissolved in aqueous caustic potash on boiling, and the solution, after acidifying and extracting with ether, yielded a solid acid which crystallised from hydrochloric acid, melted at 141—142°, and consisted of pure *as-dimethylsuccinic acid*:

0.1584 gave 0.2865 CO<sub>2</sub> and 0.0966 H<sub>2</sub>O. C = 49.4; H = 6.8.

C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> requires C = 49.3; H = 6.9 per cent.

In order to be sure of the identity of this acid, some of the anhydride was dissolved in benzene and the solution mixed with aniline, when the anilic acid separated at once in needles which, after recrystallising from dilute alcohol, melted at  $187^{\circ}$  with decomposition. Auwers (*Annalen*, 1896, 292, 186) gives the melting point of dimethylsuccinanilic acid as  $189^{\circ}$ . Some of the anilic acid was heated at  $210^{\circ}$  until the evolution of gas had ceased, and the residue recrystallised from dilute alcohol, when colourless needles were obtained which melted at  $87^{\circ}$  and gave on analysis the following results :

0.217 gave 13.4 c.c. of nitrogen at  $18^{\circ}$  and 760 mm.  $N = 7.1$ .

*Dimethylsuccinanil*,  $C_{12}H_{13}O_2N$  requires  $N = 6.9$  per cent.

The melting point of this substance is, according to Auwers (*loc. cit.*),  $84-86^{\circ}$ . It was found that the amount of dimethylsuccinic acid which was formed during the fusion varied considerably in different experiments.

#### $\alpha$ -Camphylic Acid, $C_8H_{11}\cdot CO_2H$ .

Of the isomeric camphylic acids, the  $\alpha$ -acid is easily obtained in a pure state owing to the facility with which it crystallises from acetic acid. It melts at  $148^{\circ}$ , and, as explained in the introduction, is obviously identical with the compound of the same melting point which Kachler first prepared in 1872 (*Annalen*, 1873, 169, 183):

0.1079 gave 0.2804  $CO_2$  and 0.0760  $H_2O$ .  $C = 70.9$ ;  $H = 7.8$ .

0.1765 „ 0.4852  $CO_2$  „ 0.1250  $H_2O$ .  $C = 70.8$ ;  $H = 7.9$ .

$C_8H_{12}O_2$  requires  $C = 71.0$ ;  $H = 7.9$  per cent.

$\alpha$ -Camphylic acid is readily soluble in hot ethyl and methyl alcohols, benzene, light petroleum, and glacial acetic acid, but is rather sparingly soluble in methyl alcohol and light petroleum in the cold. It crystallises from all the above solvents in glistening, striated, four-sided plates, the crystals from light petroleum being especially well-defined. It is almost insoluble in cold water, but when the finely divided substance is boiled with water, an appreciable quantity dissolves and crystallises out on cooling.

$\alpha$ -Camphylic acid is readily volatile in steam and distils under the ordinary pressure almost without decomposition at  $248^{\circ}$  (740 mm.). It is readily oxidised by nitric acid, and its solution in sodium carbonate instantly decolorises permanganate with the formation of *trihydroxy-dihydro- $\alpha$ -camphylic acid* (see p. 855).

A neutral solution of the ammonium salt gives with copper sulphate a light blue and with lead acetate a white precipitate, but no precipitate with either barium or calcium chloride even on boiling.

*Chloride of  $\alpha$ -Camphylic Acid,  $C_8H_{11}\cdot COCl$ .*

This substance was prepared by heating  $\alpha$ -camphylic acid with phosphorus trichloride on the water-bath for about half an hour and then fractionating the product. The fraction 138—140° (60 mm.) consists of the chloride of  $\alpha$ -camphylic acid :

0.1947 gave 0.1679 AgCl.  $Cl = 21.3$ .

$C_9H_{11}OCl$  requires  $Cl = 20.8$  per cent.

When left in contact with water, this chloride is gradually decomposed, yielding crystals of  $\alpha$ -camphylic acid.

*Anilide of  $\alpha$ -Camphylic Acid,  $C_8H_{11}\cdot CO\cdot NH\cdot C_6H_5$ .*

This crystalline derivative is readily obtained by adding the chloride to an excess of an ethereal solution of aniline. A vigorous reaction takes place, and after two hours the ethereal solution is washed with dilute hydrochloric acid to remove excess of aniline, then with sodium carbonate, dried over calcium chloride, and evaporated. The solid residue, when crystallised from dilute alcohol, is obtained in the form of thick, colourless prisms which melt at 111—112° :

0.2337 gave 13.2 c.c. nitrogen at 20° and 761 mm.  $N = 6.4$ .

$C_{15}H_{17}ON$  requires  $N = 6.2$  per cent.

This anilide is moderately readily hydrolysed by alcoholic potash, and the alkaline solution, on acidifying, gives a crystalline precipitate of pure  $\alpha$ -camphylic acid.

*Ester of Camphylic Acid,  $C_8H_{11}\cdot CO_2\cdot C_2H_5$ .*

This ester was prepared from the chloride by mixing it with alcohol and heating to boiling for a few minutes. On the addition of water, an oil was precipitated which, after extracting with ether and washing with sodium carbonate, distilled constantly at 132° (70 mm.) :

0.1051 gave 0.2816  $CO_2$  and 0.088  $H_2O$ .  $C = 73.1$  ;  $H = 9.2$ .

$C_{11}H_{16}O_2$  requires  $C = 73.3$  ;  $H = 8.9$  per cent.

The solution of this ester in chloroform takes up bromine at once without the evolution of hydrogen bromide.



*Action of Hydrogen Bromide on  $\alpha$ -Camphylic Acid. Formation of  $\alpha$ -Camphylic Acid Dihydrobromide (Dibromotetrahydro- $\alpha$ -camphylic Acid),*  
 $C_8H_{13}Br_2 \cdot CO_2H$ .

In preparing this interesting substance, pure  $\alpha$ -camphylic acid (3 grams) was dissolved in 10 c.c. of acetic acid and then mixed with 10 c.c. of a saturated solution of hydrogen bromide in acetic acid.

After remaining for two days in the dark, the glistening, prismatic crystals which had separated were collected at the pump and left in contact with porous porcelain in a desiccator until dry.

The crystals then melted at  $152^\circ$  with vigorous evolution of gas, and, after rapidly recrystallising from light petroleum (b.p.  $100$ — $105^\circ$ ), the melting point was  $156^\circ$ :

0.4137 gave 0.4925 AgBr. Br = 50.7.

$C_8H_{12}O_2 \cdot 2HBr$  requires Br = 50.9 per cent.

This dihydrobromide appears to decompose in moist air into  $\alpha$ -camphylic acid and hydrogen bromide, and when distilled in steam it is completely dissociated, crystals of this acid separating from the distillate. Boiling with quinoline also very quickly brings about the same decomposition.

*Action of Bromine on  $\alpha$ -Camphylic Acid. Formation of Dibromodihydro- $\alpha$ -Camphylic Acid,  $C_8H_{11}Br_2 \cdot CO_2H$ , Tribromodihydro- $\alpha$ -camphylic Acid,  $C_8H_{10}Br_3 \cdot CO_2H$ , and Monobromo- $\alpha$ -camphylic Acid,  $C_8H_{10}Br \cdot CO_2H$ .*

When  $\alpha$ -camphylic acid, dissolved in chloroform, is gradually mixed with rather more than the amount of bromine necessary to form the addition product  $C_8H_{12}Br_2O_2$ , and the solution kept in the dark at  $0^\circ$ , the bromine is slowly absorbed, and if, after the reaction is finished, the product is poured into a dish and allowed to evaporate spontaneously, a solid, crystalline cake remains. This is best purified by rubbing with light petroleum, which removes much oil, filtering, and crystallising the residue from light petroleum (b.p.  $80$ — $100^\circ$ ), this operation being rapidly carried out, as otherwise considerable decomposition takes place.

Another good method of rapidly preparing small quantities of the dibromo-acid is the following. Two grams of  $\alpha$ -camphylic acid are dissolved in 15 c.c. of glacial acetic acid and 2.2 grams of bromine in 5 c.c. of acetic acid then gradually added. The colour disappears slowly, and after two days about 0.6 gram of needle-shaped crystals will have separated, which melt at about  $165$ — $170^\circ$  with decomposition and evolution of gas, and consist of pure dibromodihydro- $\alpha$ -camphylic acid. If the mother liquors of these crystals are exposed over caustic

potash in a vacuum desiccator, a further crop of the dibromo-acid is obtained, but in a less pure condition. The analysis of the dibromo-acid gave the following results :

0.2247 gave 0.271 AgBr. Br = 51.3.

$C_9H_{12}O_2Br_2$  requires Br = 51.3 per cent.

*Dibromodihydro- $\alpha$ -camphylic acid* melts at about 165—170° with decomposition, and when heated in a test-tube is decomposed, with elimination of hydrogen bromide and formation of a volatile oil. It is readily soluble in alcohol, ether, and boiling light petroleum, moderately so in chloroform, but dissolves very sparingly in cold light petroleum; it is insoluble in cold water and when boiled with water it decomposes with separation of hydrogen bromide and evolution of much carbon dioxide.

In investigating this reaction, the pure dibromo-acid (30 grams) was heated on the water-bath with 300 c.c. of water for half an hour with constant stirring. After allowing to cool, the solid cake was warmed with dilute sodium carbonate, filtered from a volatile oil which had a strong odour of peppermint, the solution boiled with animal charcoal, and acidified, when a colourless, crystalline mass separated which, after crystallising from dilute acetic acid, melted at 148° and consisted of  $\alpha$ -camphylic acid. Two grams only of this acid were obtained in this way, the principal products of the reaction being the volatile oil just mentioned and substances soluble in water. On evaporating the aqueous solution, a yellow oil was left which had a strong odour of acetic acid, but from which nothing crystalline could be isolated.

When the solution of dibromodihydro- $\alpha$ -camphylic acid in glacial acetic acid is treated with zinc dust, elimination of bromine takes place and large quantities of  $\alpha$ -camphylic acid are produced.

If a solution of  $\alpha$ -camphylic acid (0.5 gram) in chloroform is mixed with bromine (1 gram) and exposed to sunlight at the ordinary temperature, the reaction proceeds differently from that described above, as much hydrogen bromide is eliminated. On allowing the chloroform solution to evaporate at the ordinary temperature, a brown solid separates which crystallises from warm acetic acid in needles.

This substance melts at about 178° with evolution of gas, and is evidently *tribromodihydro- $\alpha$ -camphylic acid* :

0.162 gave 0.2376 AgBr. Br = 61.1.

$C_9H_{11}O_2Br_3$  requires Br = 61.4 per cent.

*Monobromo- $\alpha$ -camphylic Acid*,  $C_8H_{10}Br \cdot CO_2H$ .—When dibromodihydro- $\alpha$ -camphylic acid is dissolved in glacial acetic acid and the solution heated to boiling in a reflux apparatus, hydrogen bromide is seen to be eliminated, and, as soon as this evolution has ceased, the solution, on

mixing with water, deposits a brown precipitate. In investigating this decomposition, the whole was extracted with ether, the ethereal solution washed several times in order to remove as much acetic acid as possible, dried over calcium chloride, and evaporated, when a dark semi-solid residue was obtained which, when dried in contact with porous porcelain, assumed a pale ochre colour. This crystallised from light petroleum in glistening plates, melted at  $107^{\circ}$ , and consisted of pure *monobromo- $\alpha$ -camphylic acid* :

0.1476 gave  $0.2560 \text{ CO}_2$  and  $0.065 \text{ H}_2\text{O}$ .  $\text{C} = 47.3$  ;  $\text{H} = 5.0$ .

0.2346 „  $0.1911 \text{ AgBr}$ .  $\text{Br} = 34.9$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{Br}$  requires  $\text{C} = 46.7$  ;  $\text{H} = 4.7$  ;  $\text{Br} = 34.6$  per cent.

*Conversion of  $\alpha$ -Camphylic Acid,  $\text{C}_8\text{H}_{11}\cdot\text{CO}_2\text{H}$ , into Inactive  $\alpha$ -Campholytic Acid,  $\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{H}$ , by Reduction with Sodium Amalgam.*

This interesting reduction may be carried out in the following way.  $\alpha$ -Camphylic acid, in quantities of not more than 10 grams, is dissolved in dilute aqueous caustic soda and 2 kilos. of 3 per cent. sodium amalgam added in four separate quantities, the liquid being kept just at the boiling point during the whole process and small quantities of water poured in from time to time to make up for the loss due to evaporation. It was found necessary to carry out the reduction at the boiling point because preliminary experiments had shown that the acid is only very slowly and incompletely reduced by sodium amalgam at the ordinary temperature.

The alkaline product is acidified, extracted with ether, the ethereal solution evaporated, and the residual oil again treated with sodium amalgam exactly as before. On subsequent fractionation, about 60 per cent. of the oily acid distils at  $160$ — $170^{\circ}$  (45 mm.), leaving a viscid residue in the flask which is described on p. 855. The distillate, when again fractionated, boiled almost constantly at  $160$ — $162^{\circ}$  as a colourless, inactive oil, a sample of which, on analysis, gave the following results :

0.1393 gave  $0.3585 \text{ CO}_2$  and  $0.1166 \text{ H}_2\text{O}$ .  $\text{C} = 70.2$  ;  $\text{H} = 9.3$ .

0.1485 „  $0.3792 \text{ CO}_2$  „  $0.1206 \text{ H}_2\text{O}$ .  $\text{C} = 69.7$  ;  $\text{H} = 9.1$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.1$  ;  $\text{H} = 9.1$  per cent.

That this acid is inactive  $\alpha$ -campholytic acid, that is to say, the inactive modification of the acid which was obtained by Walker (*Trans.*, 1893, 63, 498) by the electrolysis of the potassium salt of the *o*-ethyl ester of camphoric acid and by Noyes (*Amer. Chem. Journal*, 1894, 16, 502) by the action of nitrous acid on  $\beta$ -camphoramic acid, is shown by the examination of its properties.



*Action of Bromine.*—When the solution of the oily acid in dry chloroform was cooled to  $-10^{\circ}$  and a slight excess of bromine added drop by drop, the colour disappeared instantly and the liquid, exposed to the air in a shallow basin, deposited a crystalline solid. This was freed from moisture and oily impurity by contact with porous porcelain and then rapidly recrystallised from petroleum (b. p.  $60-70^{\circ}$ ) when colourless, microscopic crystals were obtained which evidently consisted of the *dibromide of inactive  $\alpha$ -campholytic acid*:

0.2122 gave 0.2546 AgBr. Br = 51.0.

$C_9H_{14}O_2Br_2$  requires Br = 50.9 per cent.

The melting point of this dibromide was not sharp; it softened at  $110^{\circ}$  and was completely melted at  $116^{\circ}$ . Walker (*loc. cit.*) gives  $110^{\circ}$  as the melting point of the dibromide of the active acid and Noyes (*Ber.*, 1895, 28, 552), who also prepared this substance, found  $110-114^{\circ}$  as the melting point.

*Action of Hydrobromic Acid.*—A small quantity of the reduction product of  $\alpha$ -camphylic acid was mixed with five times its volume of fuming hydrobromic acid (saturated at  $0^{\circ}$ ), in which it first dissolved and then separated as an oil which rapidly solidified. The crystals were thoroughly washed with water, left in contact with porous porcelain until dry, and then washed first with formic acid (sp. gr. 1.22) and then with a small amount of light petroleum. The white, crystalline mass of the *hydrobromide of inactive  $\alpha$ -campholytic acid* (inactive bromodihydro- $\alpha$ -campholytic acid) melted at about  $100^{\circ}$ :

0.1820 gave 0.1434 AgBr. Br = 33.6.

$C_9H_{15}O_2Br$  requires Br = 34.0 per cent.

Noyes (*loc. cit.*), who first prepared the active modification of this substance, states that it melts at  $98-100^{\circ}$ .

In an experiment made with the object of purifying this very unstable hydrobromide by recrystallisation, a considerable quantity was dissolved in formic acid (sp. gr. 1.22) at  $35-40^{\circ}$  and the solution allowed to remain over caustic potash in a vacuum desiccator for two days. The crystals, which had separated, melted at  $130^{\circ}$  and consisted of pure  $\beta$ -campholytic acid, an interesting observation which shows that the fundamental intramolecular change which occurs when  $\alpha$ -campholytic acid is converted into  $\beta$ -campholytic acid (p. 840 and below) may even take place at practically the ordinary temperature.

*Action of Dilute Sulphuric Acid.*—Two grams of the reduction product of  $\alpha$ -camphylic acid were digested with 10 grams of 30 per cent. sulphuric acid for an hour when, on remaining overnight, the oily layer had almost completely solidified. The crystals, after draining on porous porcelain, and recrystallisation from dilute

acetic acid, melted at  $128-130^{\circ}$  and consisted of  $\beta$ -campholytic acid (isolauronic acid).

0.1477 gave 0.3784  $\text{CO}_2$  and 0.1226  $\text{H}_2\text{O}$ .  $\text{C} = 69.9$ ;  $\text{H} = 9.2$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.1$ ;  $\text{H} = 9.1$  per cent.

Conversion into  $\beta$ -campholytic acid, on boiling with dilute sulphuric acid, is one of the most characteristic properties of ordinary active  $\alpha$ -campholytic acid, loss of activity taking place during the operation. It is this change, in particular, which clearly proves that the reduction product of  $\alpha$ -camphylic acid is the inactive modification of  $\alpha$ -campholytic acid.

### *Polymeride of Inactive $\alpha$ -Campholytic Acid.*

It is stated above that when  $\alpha$ -camphylic acid is reduced with sodium amalgam and the product fractionated only about 60 per cent. of inactive  $\alpha$ -campholytic acid is obtained, and there remains in the retort a transparent, yellow resin. This distils without much decomposition at  $270-290^{\circ}$  (45 mm.), and solidifies in the condenser to a resin exactly like colophony. If, however, this is dissolved in glacial acetic acid and the solution allowed to remain, hard, crystalline crusts gradually separate. The substance, which under the microscope appears to be quite homogeneous, has no definite melting point; it softens at  $205^{\circ}$ , and gradually melts as the temperature rises, and repeated recrystallisation did not affect this behaviour. The analysis of two different specimens gave the following results:

0.1250 gave 0.3218  $\text{CO}_2$  and 0.0981  $\text{H}_2\text{O}$ .  $\text{C} = 70.0$ ;  $\text{H} = 8.7$ .

0.1561 „ 0.4041  $\text{CO}_2$  „ 0.1197  $\text{H}_2\text{O}$ .  $\text{C} = 70.6$ ;  $\text{H} = 8.5$ .

$(\text{C}_9\text{H}_{14}\text{O}_2)_2$  requires  $\text{C} = 70.1$ ;  $\text{H} = 9.1$  per cent.

Probably this substance, which is an acid and readily soluble in sodium carbonate, is a condensation product of 2 molecules of  $\alpha$ -campholytic acid. It should be mentioned that Walker (*loc. cit.*) also noticed that a resinous substance, evidently similar to the above, was left in the retort when crude active  $\alpha$ -campholytic acid was submitted to fractionation.

### *Oxidation of $\alpha$ -Camphylic Acid with Permanganate. Formation of Trihydroxydihydro- $\alpha$ -camphylic Acid, $\text{C}_8\text{H}_{10}(\text{OH})_3\cdot\text{CO}_2\text{H}$ .*

In studying this oxidation,  $\alpha$ -camphylic acid (5 grams) was dissolved in dilute sodium carbonate, and, after dilution with water to 1 litre, a quantity of powdered ice was added, and then 3 per cent. permanganate solution introduced in a thin stream until the colour remained permanent. During the whole operation, a rapid stream of carbon

dioxide was maintained, and the liquid, which was always kept at  $0^{\circ}$ , vigorously stirred with a mechanical stirrer. After destroying the slight excess of permanganate by the addition of sodium sulphite, the product was heated to boiling, filtered at the pump, and the manganese precipitate well washed with hot water. The clear, yellow solution was neutralised and evaporated to a small bulk, during which operation the colour changed to dark brown. As no precipitate was formed on acidifying with hydrochloric acid, the whole was extracted 20 times with ether, the ethereal solution dried over calcium chloride and evaporated to a small bulk, when colourless, glistening crystals slowly separated. These were collected, again recrystallised from ether, and analysed, with the following results:

0.1360 gave 0.2649  $\text{CO}_2$  and 0.0836  $\text{H}_2\text{O}$ .  $\text{C} = 53.1$ ;  $\text{H} = 6.9$ .

0.1507 „ 0.2960  $\text{CO}_2$  „ 0.0934  $\text{H}_2\text{O}$ .  $\text{C} = 53.5$ ;  $\text{H} = 6.9$ .

$\text{C}_9\text{H}_{14}\text{O}_5$  requires  $\text{C} = 53.5$ ;  $\text{H} = 6.9$  per cent.

*Trihydroxydihydro- $\alpha$ -camphylic acid* softens at  $145^{\circ}$ , and decomposes rapidly at  $148$ — $150^{\circ}$  with evolution of gas and blackening; when heated in a test-tube, the substance chars, gives off an odour of burnt sugar, and yields a considerable quantity of a yellow, oily distillate. It is readily soluble in water, and a concentrated solution in warm water deposits the acid, on cooling, in colourless, glistening prisms; if, however, the aqueous solution is boiled, decomposition gradually takes place with evolution of gas and darkening, the solution ultimately becoming quite black, and, on cooling, a black resinous substance separates. The acid is sparingly soluble in chloroform, ether, benzene, and light petroleum, but very soluble in alcohol. The aqueous solution gives no precipitate with *p*-bromophenylhydrazine, and when mixed with semicarbazide hydrochloride and sodium acetate, it does not deposit crystals of a semicarbazone. That it is also incapable of yielding an oxime was shown by the fact that, after remaining in contact with hydroxylamine hydrochloride and excess of potash for 24 hours, the solution, on acidifying and extracting with ether, yielded the unchanged acid.

*Salts of Trihydroxydihydro- $\alpha$ -camphylic Acid.*—The neutral solution of the ammonium salt of the acid gives no precipitate with either silver nitrate, barium nitrate, copper sulphate, or lead acetate, and some difficulty was experienced in preparing a salt suitable for analysis, but ultimately the *barium* salt was selected for the purpose.

This was prepared by adding a slight excess of barium hydroxide to the aqueous solution of the acid, removing the excess of this alkali by passing carbon dioxide and evaporating to a small bulk, when the readily soluble barium salt slowly separated in needles.

For analysis, the salt was dried at  $100^{\circ}$  until constant, no attempt



being made to determine the water of crystallisation which appeared to be present:

0.1372 gave 0.0602  $\text{BaSO}_4$ . Ba = 25.9.

$(\text{C}_9\text{H}_{13}\text{O}_5)_2\text{Ba}$  requires Ba = 25.4 per cent.

This analysis indicates that the acid is monobasic, and in order to confirm this, a careful titration was made with decinormal caustic soda, when 0.21 gram required for neutralisation 0.0424  $\text{NaOH}$ , whereas this quantity of a monobasic acid,  $\text{C}_9\text{H}_{14}\text{O}_5$ , should neutralise 0.0416  $\text{NaOH}$ .

*Acetoxydihydroxydihydro- $\alpha$ -camphylic Acid*,  $\text{C}_8\text{H}_{12}\text{O}_2(\text{OC}_2\text{H}_5\text{O})\cdot\text{CO}_2\text{H}$ .

In preparing this acetyl derivative, the pure acid was boiled with acetic anhydride for 2 hours, and the solution placed over powdered caustic potash in a vacuum desiccator until the acetic acid and excess of acetic anhydride had evaporated. The thick, oily residue showed very little tendency to crystallise after remaining for some weeks, but when left in contact with water it was partially hydrolysed and gradually became semi-solid.

The oily impurity was easily removed by spreading on a porous plate, and subsequently extracting the hard, nearly colourless mass with boiling benzene, in which the acetyl compound is very sparingly soluble. The residue was crystallised by dissolving it in methyl alcohol, adding toluene, and boiling away the methyl alcohol; the supersaturated solution thus obtained deposited the acetyl compound in crystalline crusts:

0.111 gave 0.0684  $\text{H}_2\text{O}$  and 0.2184  $\text{CO}_2$ . C = 53.8; H = 6.8.

$\text{C}_{11}\text{H}_{16}\text{O}_6$  requires C = 54.1; H = 6.5 per cent.

That this substance, which melts at about  $185^\circ$  with decomposition, is a monoacetyl derivative was confirmed by its behaviour with decinormal caustic soda. When 0.195 gram was boiled with 50 c.c. of the alkali for 15 minutes and the excess of alkali estimated, it was found that 0.065 gram had been neutralised. On the supposition that the acetyl compound had been hydrolysed during this operation, this amount of an acid,  $\text{C}_{11}\text{H}_{16}\text{O}_6$ , becoming dibasic would neutralise 0.064  $\text{NaOH}$ .

*Oxidation of Trihydroxydihydro- $\alpha$ -camphylic Acid*.—When the aqueous solution of the acid was heated with excess of potassium dichromate and sulphuric acid in a reflux apparatus, a vigorous oxidation took place, and a distinct odour of acetone was noticed. In order to prove the presence of acetone, the product was distilled in steam and the distillate mixed with *p*-bromophenyldiazine and acetic acid, when a

crystalline precipitate separated at once. This was collected, washed, drained on a porous plate, and recrystallised from light petroleum, when groups of flat plates were obtained which melted at 95—96°, whereas the melting point of acetone *p*-bromophenylhydrazone is given as 93—94°. The chromium liquors were extracted repeatedly with ether, the ethereal solution washed with a little water, dried over calcium chloride, and evaporated, when a viscid oil was obtained which showed no signs of crystallising, even after remaining for several days over sulphuric acid in a vacuum desiccator. When this oil was distilled under 40 mm. pressure, a considerable quantity passed over at 192—205°, and this gradually deposited crystals.

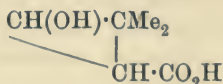
These were collected, drained on a porous plate, and purified by recrystallisation from water, from which the substance separated in colourless prisms which melted at 119—120°:

0.1171 gave 0.2366 CO<sub>2</sub> and 0.0813 H<sub>2</sub>O. C = 55.1; H = 7.7.

C<sub>6</sub>H<sub>10</sub>O<sub>3</sub> requires C = 55.4; H = 7.7 per cent.

These results agree with the formula C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>, but the substance does not appear to be identical with any known acid of this composition.

If, however, the formula for trihydroxydihydro- $\alpha$ -camphylic acid given on p. 843 is correct, it seems probable that this acid, C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>, may be a hydroxydimethyltrimethylenecarboxylic acid having the formula



Unfortunately, the amount of this acid which was obtained was so small that further investigation was impossible.

#### *Action of Bromine and Caustic Potash on $\alpha$ -Camphylic Acid.*

When the solution of  $\alpha$ -camphylic acid (12.5 grams) in excess of caustic potash is cooled to -5° and then bromine slowly added, a turbidity takes place at once, and in a short time a thick, heavy oil separates. As soon as the addition of bromine caused no further precipitation, the whole was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when an almost colourless oil (24 grams) was obtained, which, after remaining for some days over caustic potash and sulphuric acid in a vacuum desiccator, gave the following result on analysis:

0.2498 gave 0.3718 AgBr. Br = 64.6.

On acidifying the aqueous solution from which this oil had separated with sulphurous and hydrochloric acids, much carbon dioxide was

evolved, and the liquid, when extracted with ether, yielded 3.4 grams of a viscid oil which contained bromine and was not further examined. On fractionating the above-mentioned neutral oil under 25 mm. pressure, almost the whole quantity distilled at 155–160° with slight decomposition, and the distillate, which had a most pronounced odour of oil of turpentine, now furnished the following results on analysis:

0.1852 gave 0.1738  $\text{CO}_2$  and 0.0538  $\text{H}_2\text{O}$ .  $\text{C} = 25.6$ ;  $\text{H} = 3.3$ .

0.1904 „ 0.2924 AgBr.  $\text{Br} = 65.3$ .

$\text{C}_8\text{H}_{13}\text{OBr}_2$  requires  $\text{C} = 26.5$ ;  $\text{H} = 3.5$ ;  $\text{Br} = 65.8$  per cent.

This oil (18 grams) was now mixed with caustic potash (20 grams) dissolved in alcohol when, on boiling, much potassium bromide separated, and after half an hour the addition of water caused the precipitation of a heavy oil which was extracted in the usual way and weighed 11 grams. This was fractionated under 60 mm. pressure, and thus separated into two nearly equal portions which boiled at 90–100° and 130–140° respectively. The oil of lower boiling point distilled under the ordinary pressure, almost without decomposition, at 165–167°.

0.2311 gave 0.4318  $\text{CO}_2$  and 0.1222  $\text{H}_2\text{O}$ .  $\text{C} = 51.0$ ;  $\text{H} = 5.9$ .

0.2496 „ 0.2494 AgBr.  $\text{Br} = 42.5$ .

0.2665 „ 0.2672 AgBr.  $\text{Br} = 42.4$ .

$\text{C}_8\text{H}_{11}\text{Br}$  requires  $\text{C} = 51.3$ ;  $\text{H} = 5.9$ ;  $\text{Br} = 42.7$  per cent.

This oil is unsaturated and takes up bromine readily without evolution of hydrogen bromide.

The fraction of higher boiling point was also distilled under the ordinary pressure when a considerable portion passed over at 218–220°, only very slight decomposition taking place:

0.1813 gave 0.2534 AgBr.  $\text{Br} = 59.5$ .

$\text{C}_8\text{H}_{12}\text{Br}_2$  requires  $\text{Br} = 59.3$  per cent.

Damsky (*Ber.*, 1887, 20, 2961) has described a dibromide of this composition, which he obtained by brominating the hydrocarbon  $\text{C}_8\text{H}_{14}$  which results from the distillation of the ammonium salt of sulphocamphylic acid with ammonium chloride, but as he describes it as crystalline and very unstable, it cannot be identical with the dibromide described above.



*Ethyl Dibromodihydro-β-campholytate*,  $C_8H_{13}Br_2 \cdot CO_2Et$ , *Methyl Dibromodihydro-β-campholytate*,  $C_8H_{13}Br_2 \cdot CO_2Me$ , and *Ethyl Bromo-β-campholytate*,  $C_8H_{12}Br \cdot CO_2Et$ .

The ethyl dibromodihydro-β-campholytate which was required for the experiments described in the next section was prepared by dissolving ethyl β-campholytate (2·8 grams) in dry chloroform (10 grams) and then gradually adding 3·3 grams of dry bromine, the whole operation being conducted at 0° in a flask blackened by a sooty flame so as to exclude light as far as possible. After about an hour, the chloroform was removed by aspirating through the solution a stream of dry air, and the residue was then analysed with the following results :

0·2170 gave 0·2348 AgBr. Br = 46·0.

$C_{11}H_{18}O_2Br_2$  requires Br = 46·8 per cent.

*Ethyl dibromodihydro-β-campholytate*, thus prepared, is a pale yellow oil which gradually becomes dark and decomposes with evolution of hydrogen bromide.

*Methyl dibromodihydro-β-campholytate*,  $C_8H_{13}Br_2 \cdot CO_2Me$ , was also prepared in a similar manner from methyl β-campholytate and bromine. It is a yellow oil, very similar to the ethyl salt :

0·2220 gave 0·2504 AgBr. Br = 48·2.

$C_{10}H_{16}O_2Br_2$  requires Br = 48·8 per cent.

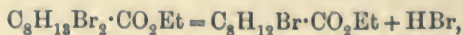
When ethyl dibromodihydro-β-campholytate is dissolved in twice its weight of glacial acetic acid and heated to boiling in a reflux apparatus, hydrogen bromide is evolved in quantity and the solution gradually darkens in colour. After digesting for an hour, the evolution of hydrogen bromide will have almost ceased; the liquid is then poured into water, extracted with ether, the ethereal solution washed with dilute sodium carbonate until free from acetic acid, dried over calcium chloride, and the ether distilled off. The residual oil distils almost constantly at 164—168° (40 mm.), and two different preparations gave the following results on analysis :

0·3275 gave 0·2258 AgBr. Br = 29·5.

0·2620 „ 0·1826 AgBr. Br = 29·7.

$C_{11}H_{17}O_2Br$  requires Br = 30·6 per cent.

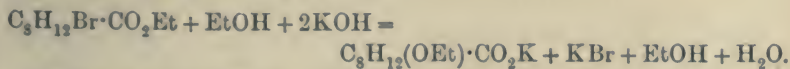
It is evident that this ester is produced from ethyl dibromodihydro-β-campholytate according to the equation



and the reaction proceeds almost quantitatively. If, then, no isomeric

change has taken place during its formation, this ester must be *ethyl bromo- $\beta$ -campholytate*.

It is evidently an ester of similar structure to bromodihydro- $\beta$ -camphylic acid (p. 847), since this acid, on heating, does not readily lose hydrogen bromide. The bromine atom in ethyl bromo- $\beta$ -campholytate is very firmly attached, and is only partly removed by boiling with diethylaniline for six hours. When, however, the ester is digested with alcoholic potash, decomposition readily takes place with separation of potassium bromide. The product from an experiment in which the ester was heated with a large excess of strong alcoholic potash for two hours was evaporated with water until free from alcohol, acidified, and repeatedly extracted with ether. The ethereal solution, after drying over calcium chloride, yielded, on evaporation, a viscid oil which distilled at  $174\text{--}177^\circ$  (35 mm.) and still contained a trace of bromine. It gave, on analysis, numbers which seem to indicate that it is *ethoxy- $\beta$ -campholytic acid*, produced according to the equation :



0.1657 gave 0.4035  $\text{CO}_2$  and 0.1316  $\text{H}_2\text{O}$ . C = 66.4 ; H = 8.7.

0.1864 „ 0.4540  $\text{CO}_2$  „ 0.1425  $\text{H}_2\text{O}$ . C = 66.5 ; H = 8.5.

$\text{C}_{11}\text{H}_{18}\text{O}_3$  requires C = 66.7 ; H = 9.1 per cent.

No further investigation of this interesting acid has, so far, been carried out.

#### *Formation of $\alpha$ -Camphylic Acid from Ethyl Dibromodihydro- $\beta$ -campholytate.*

This interesting conversion of  $\beta$ -campholytic acid into  $\alpha$ -camphylic acid, which is discussed in detail in the introduction (p. 842), was carried out as follows.

Ethyl dibromodihydro- $\beta$ -campholytate (50 grams) was heated with five times its volume of diethylaniline for six hours and the dark product poured into excess of dilute sulphuric acid and extracted five times with ether. The ethereal solution was well washed with dilute sulphuric acid, dried over calcium chloride, and the ether distilled off, when 27 grams of an oil were obtained which still contained traces of bromine. On fractionating, about two-thirds distilled at  $120\text{--}130^\circ$  (27 mm.), and under the ordinary pressure almost the whole of this passed over at  $215\text{--}216^\circ$ . The distillate was not analysed, but was at once hydrolysed by boiling with excess of alcoholic potash for three hours ; water was then added, the solution evaporated until free from alcohol, acidified, and extracted several

times with ether. The ethereal solution, after drying over calcium chloride, deposited, on evaporation, an oil which almost immediately solidified. In purifying this very crude product, it was first distilled under reduced pressure, when almost the whole quantity came over at  $192^{\circ}$  (120 mm.) as a colourless oil which at once solidified to a hard, crystalline cake, and, on recrystallising this from dilute acetic acid, a mass of glistening plates was obtained which melted at  $100-105^{\circ}$ , and which was at first thought to consist of  $\beta$ -camphylic acid (m. p.  $104^{\circ}$ ).

The behaviour of the substance on treatment with hydrogen bromide proved, however, that this was not the case. The whole mass was dissolved in acetic acid and treated with an acetic acid solution of hydrogen bromide, exactly as described on p. 851, when the solution slowly deposited glistening prisms which melted at  $150-153^{\circ}$ , and gave, on analysis, the following results:

0.3311 gave 0.3947 AgBr. Br = 50.8.

$C_9H_{14}O_2Br_2$  requires Br = 50.9 per cent.

That this dibromide, which was obtained in a yield of about 9 grams from the above quantities, was  $\alpha$ -camphylic acid dihydrobromide was proved in the following way. The finely-divided substance was digested with sodium carbonate for a few minutes and the well-cooled solution acidified, when a colourless precipitate separated which crystallised from light petroleum in glistening, four-sided plates and consisted of pure  $\alpha$ -camphylic acid, as the analysis, melting point ( $148-150^{\circ}$ ), and other properties conclusively proved:

0.1411 gave 0.3667  $CO_2$  and 0.1014  $H_2O$ . C = 70.9; H = 8.0.

$C_9H_{12}O_2$  requires C = 71.0; H = 7.9 per cent.

*$\alpha$ -Dicamphylic Acid,  $C_{16}H_{22}(CO_2H)_2$ .*

In describing the preparation and separation of the camphylic acids (p. 847), it was mentioned that the concentrated ethereal extract of the product of the fusion of sulphocamphylic acid with caustic soda sometimes deposits crystals of  $\alpha$ -dicamphylic acid. The amount of acid obtained in this way is always very small, being seldom more than 1 gram from 250 grams of the sulphonic acid, and in the case of several fusions no separation from the ethereal solution occurred at all. In all about 11.5 grams of the crude acid were collected.

This was first roughly purified by crystallisation from glacial acetic acid and the brown plates thus obtained dissolved in dilute sodium carbonate, and the solution digested with animal charcoal. The colourless acid, which was precipitated on acidifying, was crystallised from methyl



alcohol, from which it separated in needles which soften at 220—225° and melt at 230°:

0.1338 gave 0.3460  $\text{CO}_2$  and 0.0947  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 7.9$ .

0.1181 „ 0.3071  $\text{CO}_2$  „ 0.0828  $\text{H}_2\text{O}$ .  $\text{C} = 70.9$ ;  $\text{H} = 7.8$ .

$\text{C}_{18}\text{H}_{24}\text{O}_4$  requires  $\text{C} = 71.0$ ;  $\text{H} = 7.9$  per cent.

$\alpha$ -Dicamphylic acid is readily soluble in hot alcohol, benzene, and chloroform, but dissolves sparingly in light petroleum; it crystallises from glacial acetic acid in iridescent plates which contain one molecule of acetic acid of crystallisation and become opaque when heated at 100°.

0.2724 gram, heated at 100° until constant, lost 0.0448 gram of acetic acid or 16.4 per cent., whereas the formula  $\text{C}_{18}\text{H}_{24}\text{O}_4 \cdot \text{C}_2\text{H}_4\text{O}_2$  requires 16.5 per cent. of acetic acid.

The molecular weight of the acid was determined by the ebullioscopic method, using benzene as the solvent, and two experiments gave the values 313 and 298, whereas the molecular weight of  $\text{C}_{18}\text{H}_{24}\text{O}_4$  is 304. That  $\alpha$ -dicamphylic acid is a very stable substance is shown by the fact that it dissolves in concentrated sulphuric acid, forming a colourless solution, and is reprecipitated unchanged on the addition of water, and indeed, even at 100°, sulphuric acid seems to decompose the acid only very slowly. The solution of the acid in dilute sodium carbonate does not decolorise permanganate in the cold, and its solution in dry chloroform is not acted on by bromine, and therefore  $\alpha$ -dicamphylic acid is clearly a saturated acid, and in this respect especially it differs sharply from  $\alpha$ -camphylic acid, to which it is closely related (see p. 864). A probable constitutional formula for this acid is given on p. 847.

#### *Salts of $\alpha$ -Dicamphylic Acid.*

This acid dissolves readily in ammonia, but on evaporation the salt dissociates with separation of the acid, and it is possibly owing to the difficulty of preparing a neutral solution of the ammonium salt that the salts prepared did not give quite such good results on analysis as could have been wished.

The *silver* salt,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Ag}_2$ , prepared by precipitating a slightly alkaline solution of the ammonium salt with silver nitrate, is a white, gelatinous salt which, after washing with water and boiling methyl alcohol, gave the following results on analysis:

0.204 gave 0.3037  $\text{CO}_2$  and 0.0776  $\text{H}_2\text{O}$ .  $\text{C} = 40.9$ ;  $\text{H} = 4.2$ .

0.2795 „ on ignition, 0.1174 Ag.  $\text{Ag} = 42.0$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{Ag}_2$  requires  $\text{C} = 41.7$ ;  $\text{H} = 4.2$ ;  $\text{Ag} = 41.7$  per cent.

*The Calcium Salt*,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Ca} \cdot 2\text{H}_2\text{O}$  (l).—When a slightly alkaline

solution of the ammonium salt is mixed with calcium chloride, no precipitate is produced in the cold, but on boiling the calcium salt separates as a sparingly soluble, crystalline precipitate which does not redissolve in the cold. The analysis of the air-dry salt seems to indicate that it contains two molecules of water.

0.2266, when heated at  $125^{\circ}$  until constant, lost 0.0194 or 8.6 per cent., and the residue treated with sulphuric acid yielded 0.0786  $\text{CaSO}_4$ , corresponding to 10.2 per cent. of Ca.

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{Ca}, 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.5$  and  $\text{Ca} = 10.5$  per cent.

The ammonium salt of  $\alpha$ -dicamphylic acid shows the same behaviour with barium chloride as with calcium chloride, and gives with copper sulphate a pale blue, gelatinous precipitate, and with lead acetate a white, gelatinous precipitate.

*Conversion of  $\alpha$ -Dicamphylic Acid into  $\alpha$ -Camphylic Acid by Distillation.*

When  $\alpha$ -dicamphylic acid is heated in a small retort, an oil distils constantly at about  $248^{\circ}$  which solidifies in the condenser, and only a trace of residue is left in the retort. The distillate was dissolved in sodium carbonate, boiled with animal charcoal, reprecipitated, and crystallised twice from dilute acetic acid, when colourless, glistening crystals were obtained:

0.1716 gave 0.4464  $\text{CO}_2$  and 0.1241  $\text{H}_2\text{O}$ .  $\text{C} = 70.9$ ;  $\text{H} = 8.0$ .

$\text{C}_9\text{H}_{12}\text{O}_2$  requires  $\text{C} = 71.0$ ;  $\text{H} = 7.9$  per cent.

This substance melted at  $148^{\circ}$  and consisted of pure  $\alpha$ -camphylic acid, as a careful examination of its properties conclusively proved.

*Oxidation of  $\alpha$ -Dicamphylic Acid,  $\text{C}_{16}\text{H}_{22}(\text{CO}_2\text{H})_2$ . Formation of Dihydroxy- $\alpha$ -dicamphylic Acid,  $\text{C}_{16}\text{H}_{20}(\text{OH})_2(\text{CO}_2\text{H})_2$ .*

In describing the properties of  $\alpha$ -dicamphylic acid (p. 863), it was mentioned that this acid is stable to cold permanganate solution. If, however, its solution in sodium carbonate is boiled with this reagent, oxidation takes place slowly, and this reaction was carefully investigated in the hope of obtaining some further clue to the nature of  $\alpha$ -dicamphylic acid. The pure acid (3 grams) was dissolved in sodium carbonate, the solution heated to boiling, and then a cold saturated solution of 12 grams of permanganate run in drop by drop, carbon dioxide being passed through the liquid during the whole operation. The considerable excess of permanganate was destroyed by adding alcohol; the filtrate from the manganese precipitate, together with the washings evaporated to a small bulk, was acidified and extracted with

ether. The ethereal solution was dried over calcium chloride and evaporated, when a viscid, yellow oil was obtained which rapidly solidified.

On grinding with ether, an oil\* dissolved leaving a hard residue, which was collected and crystallised from dilute hydrochloric acid, from which it separated in microscopic needles :

0.1019 gave 0.2397  $\text{CO}_2$  and 0.0666  $\text{H}_2\text{O}$ .  $\text{C} = 64.1$  ;  $\text{H} = 7.2$ .

$\text{C}_{18}\text{H}_{24}\text{O}_6$  requires  $\text{C} = 64.3$  ;  $\text{H} = 7.1$  per cent.

When heated in a capillary tube, *dihydroxy- $\alpha$ -dicamphylic acid* softens at about  $245^\circ$  and melts at  $255\text{--}257^\circ$  with rapid decomposition, due to evolution of gas. It is sparingly soluble in ether and light petroleum, but readily so in water, from which it separates in spherulitic crystals. The *silver* salt,  $\text{C}_{16}\text{H}_{22}\text{O}_2(\text{CO}_2\text{Ag})_2$ , was obtained by adding silver nitrate to a neutral solution of the ammonium salt as an amorphous precipitate which slowly became sandy :

0.1890 gave 0.0740 Ag.  $\text{Ag} = 39.3$ .

$\text{C}_{18}\text{H}_{22}\text{O}_6\text{Ag}_2$  requires  $\text{Ag} = 39.2$  per cent.

*Dihydroxy- $\alpha$ -dicamphylic acid* does not yield an oxime when treated in alkaline solution with hydroxylamine, the acid being recovered by acidifying and extracting with ether. When, however, it is digested with acetic anhydride, it yields an acetyl derivative, the composition of which could not be determined with certainty owing to lack of material. When the pure acid (0.5 gram) was digested with 5 grams of acetic anhydride and the solution allowed to concentrate over powdered caustic potash in a vacuum desiccator, glistening, six-sided plates separated, which melted somewhat indefinitely at  $174\text{--}175^\circ$ , and gave, on analysis, the following results :

0.1012 gave 0.2319  $\text{CO}_2$  and 0.0636  $\text{H}_2\text{O}$ .  $\text{C} = 62.3$  ;  $\text{H} = 6.9$ .

$\text{C}_{22}\text{H}_{28}\text{O}_8$  requires  $\text{C} = 62.8$  ;  $\text{H} = 6.7$  per cent.

When boiled with water, this acetyl compound is hydrolysed into acetic acid and dihydroxy- $\alpha$ -dicamphylic acid, and it is exceedingly probable that it is a diacetyl derivative having the formula



\* This oil contained about 1 gram of unchanged  $\alpha$ -dicamphylic acid, which was isolated by conversion into the calcium salt and subsequent treatment with hydrochloric acid.



*isoBromodihydro-β-camphylic Acid*,  $C_8H_{12}Br \cdot CO_2H$ , and *β-Camphylic* *Acid*,  $C_8H_{11} \cdot CO_2H$ .

The formation of *β-camphylic acid* from chlorodihydro-*β-camphylic acid* (or bromodihydro-*β-camphylic acid* \*) by the action of alcoholic potash,  $C_8H_{12}Cl \cdot CO_2H = C_8H_{11} \cdot CO_2H + HCl$ , has already been described (Trans., 1898, 73, 826).

Most of the material used in the present research was, however, prepared by the method described on p. 847. The crude *β-camphylic acid* thus obtained usually melts at about 90—100°, and contains traces of *α-camphylic acid* and other impurities which are very difficult to remove; it may be purified by repeated recrystallisation from dilute acetic acid, but the process is exceedingly tedious. A sample which had been purified in this way, and which melted at 101—103°, gave, on analysis, the following results:

0.1718 gave 0.4438  $CO_2$  and 0.1301  $H_2O$ .  $C = 70.5$ ;  $H = 8.4$ .

$C_9H_{12}O_2$  requires  $C = 71.0$ ;  $H = 7.9$  per cent.

A simpler and more satisfactory method of purification, which, however, is attended with considerable loss, consists in first converting the crude acid into *isobromodihydro-β-camphylic acid*, which is easily obtained quite pure, and then regenerating the *β-camphylic acid* by the elimination of hydrogen bromide. The preparation of *isobromodihydro-β-camphylic acid* is as follows. Crude *β-camphylic acid* (20 grams) is dissolved in 20 c.c. of glacial acetic acid, cooled until crystallisation just commences, and then a saturated solution of hydrogen bromide in acetic acid (35 c.c.) added, and the mixture allowed to remain for two days in a cool place.

The cake of glistening crystals which will have separated is collected at the pump, drained on a porous plate, and, if necessary, further purified by rapid recrystallisation from light petroleum (b. p. 80—100°):

0.2112 gave 0.1710  $AgBr$ .  $Br = 34.4$ .

$C_9H_{13}O_2Br$  requires  $Br = 34.3$ .

\* As this decomposition has an important bearing on the question of the constitution of *β-camphylic acid*, it was again investigated and confirmed in the following way.

Bromodihydro-*β-camphylic acid* was carefully purified by repeated recrystallisation from light petroleum, when it melted at 130—131° (the previously observed melting point of a specimen crystallised from formic acid was 128—129°). This pure bromo-acid was then decomposed by alcoholic potash and the resulting acid, after crystallisation, melted at 103—104°. That this was *β-camphylic acid* was proved by analysis and by the fact that when mixed with a sample of this acid which had been prepared by the method described on p. 867, no alteration in the melting point could be observed.

*isoBromodihydro- $\beta$ -camphylic acid* melts at about  $137$ — $138^{\circ}$ , and is very sparingly soluble in light petroleum in the cold and not very readily so on boiling. When left in a vacuum desiccator over caustic potash, the acetic acid mother liquors of this substance gradually deposit a further quantity of crystals of the same bromo-acid, and the dark filtrate from these yields, on pouring into water, an ochre-coloured precipitate. This was collected, dried on porous plates, and then recrystallised from light petroleum. The feathery needles which separated were found to consist of pure *dibromotetrahydro- $\alpha$ -camphylic acid* (see pp. 843, 851).

*isoBromodihydro- $\beta$ -camphylic acid* is isomeric with the acid previously obtained by the action of heat on sulphocamphylic bromide (Trans., 1898, 73, 827), and which melts at  $130^{\circ}$ . The most striking difference between these two isomerides is their behaviour on heating. The latter is very stable and may be distilled without decomposition, whereas *isobromodihydro- $\beta$ -camphylic acid* is at once decomposed on heating with elimination of hydrogen bromide.

*Action of Water on isoBromodihydro- $\beta$ -camphylic Acid. Formation of  $\beta$ -Camphylic Acid.*

When the finely-powdered bromo-acid is mixed with water and heated on the water-bath, it rapidly melts and sinks as a heavy oil, and soon undergoes decomposition into hydrogen bromide and  $\beta$ -camphylic acid, the change being apparently a quantitative one. After half an hour, the mass is cooled, the precipitate collected, and recrystallised from dilute acetic acid, from which it separates in striated plates:

0.1440 gave 0.3730  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C} = 70.7$  ;  $\text{H} = 8.2$ .

0.1586 „ 0.4125  $\text{CO}_2$  „ 0.1144  $\text{H}_2\text{O}$ .  $\text{C} = 70.9$  ;  $\text{H} = 8.0$ .

$\text{C}_9\text{H}_{12}\text{O}_2$  requires  $\text{C} = 71.0$  ;  $\text{H} = 7.9$  per cent.

Prepared in this way,  *$\beta$ -camphylic acid* melts at about  $104^{\circ}$ , but not quite sharply, and repeated recrystallisation raises the melting point to about  $105$ — $106^{\circ}$ . It is very readily soluble in alcohol, ether, and most other organic solvents, but is very sparingly so in water. If, however, the finely-divided acid is boiled with much water, it dissolves appreciably, and the solution, after filtering, deposits, on cooling, feathery crystals of the pure acid.

It sublimes slowly at  $80$ — $90^{\circ}$ , and is readily volatile in steam ; when distilled under reduced pressure, it passes over, without any decomposition, at  $192^{\circ}$  (120 mm.), and, indeed, it may be distilled, in small quantities, under the ordinary pressure with little decomposition, the boiling point being about  $248^{\circ}$  (740 mm.). This boiling

point is exactly the same as that of  $\alpha$ -camphylic acid, and in order to be sure of this, both determinations were made on the same day and in the same apparatus.

When left in contact with light and air,  $\beta$ -camphylic acid becomes yellow, and when distilled a quantity of a dark brown resin (probably a polymeride, see p. 862), which boils at a very high temperature, is left in the retort. This behaviour has not been observed in the case of  $\alpha$ -camphylic acid.

The solution of the acid in sodium carbonate decolorises permanganate instantaneously.

*Salts of  $\beta$ -Camphylic Acid.*—The silver salt,  $C_8H_{11}\cdot CO_2Ag$ , is obtained as a white, distinctly crystalline precipitate when silver nitrate is added to a slightly alkaline solution of the ammonium salt.

It is not readily acted on by light, and when heated in a test-tube it yields a yellow, oily distillate, which solidifies on cooling :

0.2372 gave 0.3610  $CO_2$ , 0.0938  $H_2O$ , and 0.0992 Ag.  $C=41.5$  ;  
 $H=4.4$  ;  $Ag=41.8$ .

$C_9H_{11}O_2Ag$  requires  $C=41.7$  ;  $H=4.3$  ;  $Ag=41.7$  per cent.

The neutral solution of the ammonium salt gives white, amorphous precipitates with lead, zinc, and cadmium chlorides, a pale green precipitate with copper acetate, but the barium and calcium salts are readily soluble in water.

$\beta$ -Camphylic acid differs sharply from the isomeric  $\alpha$ -acid (p. 853) in that it does not appear to be capable of being reduced by means of sodium amalgam. The pure acid (5 grams) was dissolved in dilute aqueous caustic soda, a large excess of freshly prepared sodium amalgam was added in small quantities at a time, the solution being heated to boiling during the whole operation and until the amalgam was decomposed. On acidifying, a white crystalline acid separated, which, after crystallising from dilute acetic acid, melted at  $104-106^\circ$ , and consisted of unchanged  $\beta$ -camphylic acid :

0.1226 gave 0.3190  $CO_2$  and 0.0866  $H_2O$ .  $C=70.9$  ;  $H=7.9$ .

$C_9H_{12}O_2$  requires  $C=71.0$  ;  $H=7.9$  per cent.

As this behaviour was difficult of explanation, the experiment was repeated, but exactly the same result was obtained.\*

\* Since  $\beta$ -campholytic acid is the principal product obtained when sulphocamphylic acid is fused with caustic soda in a cast iron vessel (Trans., 1898, 73, 829), it seems probable that both  $\alpha$ - and  $\beta$ -camphylic acids are reduced to  $\beta$ -campholytic acid by the action of iron at the high temperature of the fusion.



*Methoxydihydro- $\beta$ -camphylic Acid*,  $C_8H_{12}(OMe) \cdot CO_2H$ .

It has just been stated that when *isobromodihydro- $\beta$ -camphylic acid* is boiled with water it is readily decomposed with formation of  $\beta$ -camphylic acid, and it is therefore remarkable that, when digested with methyl-alcoholic potash, the reaction should proceed in quite a different direction with the formation of *methoxydihydro- $\beta$ -camphylic acid* :



*isoBromodihydro- $\beta$ -camphylic acid* (5 grams) was dissolved in a solution of caustic potash (5 grams) in absolute methyl alcohol, when potassium bromide began to separate at once, the liquid becoming quite warm.

After boiling for a few minutes on the water-bath, water was added and the solution evaporated until free from methyl alcohol.

On acidifying, an oil was deposited which was extracted with ether, the ethereal solution dried over calcium chloride and evaporated, when an oily residue was obtained which soon began to crystallise, and on remaining overnight became almost solid. In contact with porous porcelain, the oily impurity was gradually absorbed, and the residue, after washing with a little light petroleum and crystallising from the same solvent, was obtained in the form of hard, glistening, crystalline crusts, which melted at  $94^\circ$  :

0.1436 gave 0.3049  $CO_2$  and 0.1128  $H_2O$ .  $C = 64.8$  ;  $H = 8.7$ .

0.1584 ,, 0.3781  $CO_2$  ,, 0.1248  $H_2O$ .  $C = 65.1$  ;  $H = 8.8$ .

$C_{10}H_{16}O_3$  requires  $C = 65.2$  ;  $H = 8.7$  per cent.

*Methoxydihydro- $\beta$ -camphylic acid* is very readily soluble in alcohol, benzene, and hot light petroleum, and is a saturated acid, since its solution in sodium carbonate does not reduce permanganate.

The *silver salt*,  $C_8H_{12}(OMe) \cdot CO_2Ag$ , prepared by precipitating the neutral solution of the ammonium salt with silver nitrate, was a sparingly soluble, caseous precipitate :

0.1833 gave 0.2760  $CO_2$  ; 0.0829  $H_2O$ , and 0.0675 Ag.  $C = 41.0$  ;  
 $H = 5.0$  ;  $Ag = 36.8$ .

$C_{10}H_{15}O_3Ag$  requires  $C = 41.2$  ;  $H = 5.1$  ;  $Ag = 37.1$  per cent.

The neutral solution of the ammonium salt gives no precipitate with barium or calcium chloride, but copper sulphate produces a bluish-green, caseous precipitate.

The constitution of this acid may, of course, be easily deduced from that of *isobromodihydro- $\beta$ -camphylic acid* (p. 847) by substituting the methoxy-group for the bromine atom in that formula.

*Dibromodihydro-β-camphylic Acid*,  $C_8H_{11}Br_2 \cdot CO_2H$ , and *Bromo-γ-camphylic Acid*,  $C_8H_{10}Br \cdot CO_2H$ .

β-Camphylic acid reacts very readily with bromine, the addition taking place almost quantitatively in chloroform solution, as the following experiment shows. Two grams of the acid, dissolved in chloroform, decolorised 2.04 grams of bromine, whereas, according to the equation  $C_8H_{11} \cdot CO_2H + Br_2 = C_8H_{11}Br_2 \cdot CO_2H$ , 2.1 grams of bromine should have been absorbed.

The product was allowed to remain on a flat watch-glass until the chloroform had evaporated, and the crystalline residue ground up with light petroleum to remove a slight trace of oily impurity, and then rapidly recrystallised, first from the same solvent and then from benzene. The *dibromodihydro-β-camphylic acid* separates from benzene in glistening plates, which melt at about 172° with rapid decomposition:

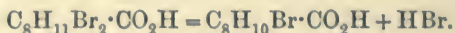
0.2120 gave 0.2531 AgBr. Br = 50.8.

$C_9H_{12}O_2Br_2$  requires Br = 51.2 per cent.

A more convenient way of preparing small quantities of this dibromo-acid is the following:

β-Camphylic acid (1 gram) is dissolved in a little glacial acetic acid and treated with bromine (1.1 grams), dissolved in acetic acid; a quantity of crystals of the pure dibromo-acid slowly separates. The filtrate from these crystals, if left over powdered caustic potash in a desiccator, deposits a crust of the same acid which, if washed with a little acetic acid to remove a slight amount of oily impurity, melts at 168–170° with decomposition and is almost pure.

Dibromodihydro-β-camphylic acid is readily soluble in alcohol and in hot benzene, but almost insoluble in cold light petroleum. When heated in a test-tube, it decomposes with evolution of much hydrogen bromide, and the residue distils almost completely as a pale-green oil which solidifies on stirring. When either treated in the cold with alcoholic caustic potash or boiled with acetic acid or diethylaniline, it loses hydrogen bromide, and is converted into bromo-γ-camphylic acid,



*Expt. I.*—The dibromo-acid (1 gram) was heated with diethylaniline (5 grams) just to boiling, the product was then poured into dilute hydrochloric acid, and the precipitate collected, dissolved in sodium carbonate, and boiled with animal charcoal. The colourless filtrate was acidified, and the precipitate recrystallised from light petroleum, when glistening plates were obtained which melted at 148–152° and consisted of *bromo-γ-camphylic acid*:

0.1790 gave 0.3076  $\text{CO}_2$  and 0.0806  $\text{H}_2\text{O}$ .  $\text{C} = 46.8$ ;  $\text{H} = 5.0$ .  
 0.2608 „ 0.2108  $\text{AgBr}$ .  $\text{Br} = 34.4$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{Br}$  requires  $\text{C} = 46.7$ ;  $\text{H} = 4.7$ ;  $\text{Br} = 34.6$  per cent.

*Expt. II.*—The dibromo-acid (5 grams) was dissolved in 50 grams of glacial acetic acid and heated to boiling in a reflux apparatus, when much hydrogen bromide was eliminated, and as soon as this ceased to be given off, the product was poured into water and allowed to remain overnight. The brown, crystalline precipitate was purified by treating its solution in sodium carbonate with animal charcoal, and subsequently recrystallising the acid from light petroleum exactly as in *Expt. I*. The bromo-acid thus obtained softened at about  $146^\circ$ , melted at  $152^\circ$ , and gave the following results on analysis :

0.1142 gave 0.0928  $\text{AgBr}$   $\text{Br} = 34.6$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{Br}$  requires  $\text{Br} = 34.6$  per cent.

*Expt. III.*—The following is perhaps the most convenient process for preparing bromo- $\gamma$ -camphylic acid. The dibromo-acid is dissolved in cold methyl alcohol and mixed with an excess of a filtered solution of methyl-alcoholic potash. In a short time, the liquid becomes cloudy, owing to the separation of potassium bromide, and after an hour the whole is heated just to boiling and then poured into excess of dilute hydrochloric acid. The colourless, crystalline mass which separates is then recrystallised, when it melts at about  $152^\circ$ , and is identical with the acid obtained by either of the two processes described above.

*Bromo- $\gamma$ -camphylic acid* is readily soluble in hot, but only sparingly so in cold light petroleum; it dissolves readily in alcohol and benzene, but is almost insoluble in water, even on boiling.

The bromine atom in this acid is very firmly attached, since it is only very slowly eliminated on boiling with caustic potash, and the acid remains unchanged when its alcoholic solution is digested with zinc dust and acetic acid. Again, when dissolved in sodium carbonate and treated with a large excess of sodium amalgam, the unchanged acid separates on acidifying. The formula assigned to this acid on p. 847 affords a ready explanation of the remarkable stability which this bromo-acid exhibits, especially towards alkalis, as, according to this formula, there is no adjacent hydrogen atom with which the bromine atom can combine to form hydrogen bromide.

#### *Oxidation of $\beta$ -Camphylic Acid.*

In investigating this oxidation, 10 grams of the pure acid were dissolved in dilute sodium carbonate and treated with permanganate at  $0^\circ$  in the presence of carbon dioxide, exactly as described in the case of  $\alpha$ -camphylic acid (p. 855). Since, after concentrating and



acidifying, ether only extracted a portion of the product, the whole was evaporated to dryness and extracted with ether in a Soxhlet apparatus. The ethereal solution was dried over calcium chloride and evaporated, when a viscid syrup was obtained which, even after remaining some days over sulphuric acid in a vacuum desiccator, showed no signs of crystallising, and which on analysis gave numbers agreeing closely with those required by the formula  $C_9H_{14}O_5$ . Two different preparations were analysed with the following results:

0.1391 gave 0.2732  $CO_2$  and 0.0942  $H_2O$ .  $C = 53.5$ ;  $H = 7.5$ .

0.1803 „ 0.3512  $CO_2$  „ 0.1219  $H_2O$ .  $C = 53.1$ ;  $H = 7.5$ .

$C_9H_{14}O_5$  requires  $C = 53.5$ ;  $H = 6.9$  per cent.

On titration, the substance gave results which show that it is a monobasic acid. 0.4906 gram dissolved in water neutralised 0.134 gram KOH, whereas this amount of a monobasic acid,  $C_9H_{14}O_5$ , should neutralise 0.136 gram KOH. This acid is probably a *ketodihydroxy-dihydro- $\beta$ -camphylic acid* having the formula given on p. 845.

This syrupy acid was now dissolved in water and digested with sodium dichromate and sulphuric acid until no further action took place. On distilling the product in steam, the odour of acetone was very noticeable, and the first portions of the distillate gave, with *p*-bromophenylhydrazine acetate, a copious precipitate of acetone *p*-bromophenylhydrazone (m. p.  $93^\circ$ ). The residue was saturated with ammonium sulphate and repeatedly extracted with ether and the ethereal solution evaporated, when an oil was obtained which smelt of acetic acid, and which after some months, became semi-solid owing to the separation of a quantity of needle-shaped crystals. These were freed from the oily mother liquor by contact with porous porcelain, and then crystallised from hydrochloric acid, when colourless crystals were obtained which melted at  $140^\circ$ , and consisted of  $\alpha\alpha$ -dimethylsuccinic acid,  $CO_2H \cdot CMe_2 \cdot CH_2 \cdot CO_2H$ :

0.1561 gave 0.2809  $CO_2$  and 0.0985  $H_2O$ .  $C = 49.1$ ;  $H = 7.0$ .

$C_6H_{10}O_4$  requires  $C = 49.3$ ;  $H = 6.9$  per cent.

This acid yielded the characteristic calcium salt, and its identity with  $\alpha\alpha$ -dimethylsuccinic acid was further demonstrated by mixing it with a sample of this acid which had been prepared from ethyl malonate, when no alteration in the melting point could be observed.

In conclusion, the author wishes to state that much of the heavy expense incurred in carrying out this investigation has been met by repeated grants from the Research Fund of the Royal Society.

LXXXVI.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part VIII. Resolution of the  $\alpha$ -Modification of Hydrindamine Bromocamphorsulphonate.*

By FREDERIC STANLEY KIPPING.

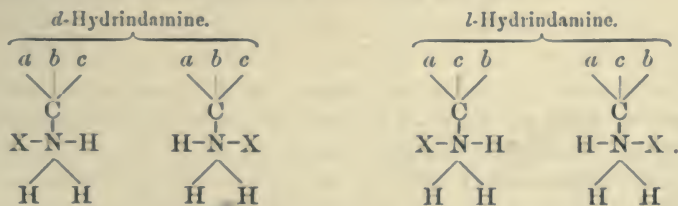
IN parts I—VII of this series of papers (Trans., 1900, 77, 861; 1901, 79, 430), the author has described the isolation and properties of several pairs of isomeric salts, distinguished as  $\alpha$ - and  $\beta$ -salts, which he obtained by the combination of *dl*-hydrindamine with *d*-bromo- and *d*-chloro-camphorsulphonic acids, and with *cis*- $\pi$ -camphanic acid, and also by the combination of benzylhydrindamine with the *d*-bromo-acid. The facts established in the investigation of these compounds led to the conclusion that in every case both the isomeric salts contain an externally compensated base; consequently, any explanation of their isomerism based on the assumption that the resolution of the base had occurred was to be regarded as untenable.

This limitation imposed the necessity of advancing some other explanation of the existence of such isomerides, which were apparently of a type previously unknown, and after a consideration of all the facts (*loc. cit.*), the view embodied in the following statements was provisionally adopted:

(a) The two unoccupied valencies of the quinquevalent nitrogen atom of an amino-group, which is a component of an optically active compound, cannot be identically situated with regard to the molecule as a whole.

(b) When such an amino-group combines with the ions of an acid, union may take place in two ways, thus giving rise to isomeric salts.

(c) An externally compensated base such as hydrindamine might therefore give rise to four different salts, two being formed from the *d*- and two from the *l*-modification, as indicated below:



(d) These four compounds might then unite in pairs to produce isomeric partially racemic salts such as the  $\alpha$ - and  $\beta$ -modifications of hydrindamine bromocamphorsulphonate.

According to this view, each of the isomeric salts consists of two components, one derived from *d*-hydrindamine, the other from the enantiomorphously related *l*-base, and, further, each optically active base, if isolated, should give two different salts when combined with the *d*-acid; both these deductions have now been established experimentally, and the further study of these and of similar compounds thus seems to point to the existence of isomeric nitrogen compounds of the type  $\text{NR}_1\text{R}_2\text{H}_3$ .

The present paper, part VIII, contains an account of the resolution of the partially racemic  $\alpha$ -salt, obtained from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid, into the salts of the *d*- and *l*-bases; although, for reasons which will appear later, it is difficult to decide which should be regarded as the dextro- and which as the lævo-rotatory base, these two components of the  $\alpha$ -salt may be distinguished as the *ad*- and *al*-isomerides respectively; the partially racemic  $\alpha$ -salt then is a crystalline combination of equal or approximately equal quantities of these isomerides.

The resolution of the partially racemic  $\alpha$ -salt is accomplished with the aid of ethyl acetate under special conditions. As previously stated (*Trans.*, 1900, 77, 861), this salt may be repeatedly crystallised fractionally from warm or cold water, dilute alcohol, or dilute acetone without undergoing any appreciable change, and crystallisation from warm ethyl acetate under ordinary conditions also fails to resolve it into its components; when, however, crystallisation is carried out at the boiling point of the solution, the latter deposits the *ad*-salt, and the mother liquors give *al*-salt, together with a large proportion of unchanged  $\alpha$ -salt, which is separated and treated again.

The *ad*- and *al*-salts are easily obtained in a state of purity; they both crystallise in anhydrous prisms (the partially racemic  $\alpha$ -salt contains 5.1 per cent.  $\text{H}_2\text{O}$ ) melting at about  $222^\circ$  and  $130^\circ$  respectively; they have practically the same specific rotation in aqueous solution, but in chloroform their values are very different, as shown by the following data:

|                       | $[\alpha]_D$ in water. | $[\alpha]_D$ in chloroform. | $[M]_D$ in water. |
|-----------------------|------------------------|-----------------------------|-------------------|
| <i>ad</i> -Salt.....  | +61°                   | +30°                        | +271              |
| <i>al</i> -Salt ..... | +60                    | +60                         | +266              |

The molecular rotation in aqueous solution approximates very closely to  $270^\circ$  in both cases, and, as this is the value of the molecular rotation of the acidic ion, it is obvious that the basic ions are practically devoid of optical activity; that the bases of the *ad*- and *al*-salts do actually represent the *d*- and *l*-forms of hydrindamine is proved, however, by the following facts. (1) A concentrated solution in very dilute alcohol of the base obtained from the *ad*-salt is dextro-rotatory, whilst a similar solution of the base of the *al*-salt is lævo-



rotatory. (2) The two bases give hydrochlorides, platinichlorides, and picrates which are identical in melting point, crystalline form, and other ordinary properties, but when combined with optically active acids such as *d*-bromo- and *d*-chloro-camphorsulphonic acids, *cis*- $\pi$ -camphanic acid, and Reychler's camphorsulphonic acid, they give rise to salts which differ in melting point, &c.

It is an interesting fact that in some of their salts the bases appear to be almost optically inactive and that the slight activity which the salts doubtless possess is of opposite sign to that of the bases themselves; thus, a 15 per cent. solution of the hydrochloride of that base which is dextrorotatory in aqueous alcoholic solution shows a lævorotation of  $[\alpha]_D - 0.8^\circ$ ; these observations do not, of course, throw any doubt on the enantiomorphous relationship of the bases, but they explain the closely approximating values of the molecular rotations of the *ad*- and *al*-isomerides in aqueous solution. They also show that the mere fact that the salt of an optically active acid has the same molecular rotation as the acid itself cannot be accepted as evidence that the base is not enantiomorphous; in other words, optical examination may frequently fail to distinguish between a salt of the type *dAdB* on the one hand, and a partially racemic salt on the other. The *ad*- and *al*-salts undergo no change when repeatedly crystallised from water, dilute alcohol, or other solvents, and the bases liberated from these salts do not undergo racemisation when kept at the ordinary temperature or when distilled in a current of steam, except possibly to a very minute extent, this statement being based on the fact that when the distilled base is recombined with *d*-bromocamphorsulphonic acid the resulting salt is always free from the partially racemic  $\alpha$ - and  $\beta$ -salts.

The salt thus obtained by combining the optically active base of the *ad*-compound with the *d*-bromo-acid, and which will in future be termed the *regenerated* salt, is nevertheless different from the original substance; similarly, the regenerated *al*-salt is not identical with the original one, this difference being proved in the following manner. When equal quantities of the *ad*- and *al*-salts, obtained by the resolution of the  $\alpha$ -salt, are mixed together and the product crystallised fractionally from water, all the fractions consist of the partially racemic  $\alpha$ -salt; but a mixture of regenerated *ad*- and *al*-salts, treated in the same way, gives both the  $\alpha$ - and the  $\beta$ -partially racemic salts.

This behaviour is a necessary consequence of the views already expressed, and may be regarded as affording them strong support. The suggested explanation is that each of the free optically active bases combines with the acid, giving rise to very unequal quantities of two isomeric salts; the regenerated salt of the *d*-base is a mixture of *ad* and a new isomeride,  $\beta d$ , whilst the regenerated salt of the *l*-base contains, in addition to *al*, a new isomeride,  $\beta l$ . When the

regenerated salts are mixed and crystallised, *ad* and *al* are deposited together, forming the partially racemic  $\alpha$ -salt, whilst  $\beta d$  and  $\beta l$  (together with the  $\alpha$ -forms, compare p. 890) give the partially racemic  $\beta$ -salt. As the  $\alpha$ -isomeride is produced in by far the larger proportion, and as, moreover, the *ad*- and  $\beta d$ -varieties are very similar, an ordinary series of fractional crystallisations of the regenerated salt fails to reveal the presence of the  $\beta d$ -variety, and it is probable that this isomeride has not even yet been isolated in a pure condition; in the case of the regenerated *al*-compound, however, a complete separation of the *al*- and  $\beta l$ -components is possible, and both have been carefully examined.

The results of the further investigation of the partially racemic  $\alpha$ -salt, produced from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid, in so far as they bear on this question of isomeric salts of the type  $\text{NR}_1\text{R}_2\text{H}_3$ , are fully borne out by those obtained during the study of the isomeric partially racemic  $\beta$ -salt.

#### EXPERIMENTAL.

##### *Resolution of the partially Racemic $\alpha$ -Salt.*

The partially racemic  $\alpha$ -modification of hydrindamine bromocamphorsulphonate, freed from the isomeric  $\beta$ -salt by repeated crystallisation from water, is roughly dried in the air and dissolved in a very small quantity of anhydrous ethyl alcohol; the solution is then evaporated in a beaker on the water-bath, where it is left for some time in order to expel as much water as possible and most of the alcohol.

The syrup which remains is mixed, while still hot, with anhydrous ethyl acetate, placed again on the water-bath, and the solution stirred vigorously. If too much alcohol be present, a precipitate is not produced, whereas if too much ethyl acetate be added, unchanged  $\alpha$ -salt, or what seems to be such, may be deposited, particularly if the temperature of the solution be allowed to fall; with suitable proportions of the two solvents, however (a condition which is best attained by adding the ethyl acetate in small portions at a time), the hot solution gives a deposit of minute needles, which gradually increases in quantity on leaving the solution simmering on the water-bath. This deposit, which consists of the *ad*-salt, must be rapidly separated by filtration through a hot funnel, for if the solution be allowed to cool it sets to a solid mass composed of either the partially racemic salt, or an intimate mixture of the *ad*- and *al*-components.

The original filtrate is immediately poured back into a beaker and heated again on the water-bath with the addition of a little more ethyl acetate, when a second deposit may, or may not, be obtained, accord-



ing to the manner in which the first operation has been carried out if no precipitate be produced, the addition of a little petroleum (b. p. 80—90°) will often cause the separation of a second crop of crystals identical with the first, but unless great care is taken this precipitate usually consists of a mixture of the *αl*- and *αl*-isomerides. For this reason, the use of light petroleum is not to be recommended, and if ethyl acetate fails to give a precipitate, the solution is best treated as described below.

If the resolution of the salt has been successfully accomplished, the deposit or deposits from the hot solution, after having been washed with a little boiling ethyl acetate, will melt at a temperature of about 220°, and will separate from water in long, distinct needles, free from the opaque, felted masses of the *α*-salt; if, however, the presence of the latter is detected on crystallising a test portion, it is best to redissolve the whole in the least possible quantity of boiling ethyl alcohol and again precipitate with ethyl acetate from the hot solution. The crude *αl*-salt is finally crystallised from boiling water until its melting point is constant and the aqueous mother liquors do not give the characteristic felted masses of the partially racemic salt, the presence of which is so easily recognised by inspection. The final aqueous filtrates from the *αl*-salt give deposits of this salt mixed with the partially racemic salt; these two substances can be separated mechanically to some extent, but it is best to evaporate the liquid to dryness and to treat the residue as original material.

The ethyl acetate mother liquors from the original deposit of *αl*-salt still contain a very large quantity of this compound of higher melting point, which, however, cannot be separated because the solution is also saturated with the *αl*-isomeride; when allowed to cool, it sets to a mass of crystals which seems to consist of the hydrated racemic salt mixed with an anhydrous partially racemic salt; at any rate, when this mass is separated and dissolved in water, it gives the hydrated partially racemic *α*-salt. In order to isolate the *αl*-salt, one of two methods may be adopted. (1) A few drops of water are added to the hot ethyl acetate mother liquor, and the solution is allowed to cool; the deposit of the partially racemic *α*-salt is separated, the mother liquors allowed to evaporate, and further crops of the *α* salt again removed; the filtrate is then evaporated to dryness and the residue slowly crystallised from water or very dilute alcohol; this solution deposits yellow or brown rosettes of compact needles of the *αl*-isomeride. (2) The hot ethyl acetate mother liquors are mixed with such a quantity of ethyl alcohol that crystallisation takes place only very slowly after the mixture has cooled to the ordinary temperature; the first deposits then consist principally (or entirely) of rosettes of compact, anhydrous needles of the *αl*-salt, which is finally recrystallised



from hot water; the alcoholic ethyl acetate filtrate gives, on further evaporation, the partially racemic  $\alpha$ -salt.

The partially racemic  $\alpha$ -salt obtained from the solutions by either of these methods is again treated in the same way as the original material, and a further quantity is thus resolved. By repeating these operations, practically the whole is separated into approximately equal quantities of its two components, but the final residues, on crystallisation from water, give a mixture of the  $\alpha$ -salt and partially racemic salt which cannot be easily separated.

*ad-Hydrindamine d-Bromocamphorsulphonate.*

The  $\alpha$ -salt, which is deposited from the hot ethyl acetate solution of the partially racemic  $\alpha$ -salt, crystallises from hot water in long, colourless, transparent needles, and from cold aqueous alcohol in massive, transparent prisms exceeding 20 mm. in length. It melts at 222–223°, apparently without decomposing, and is anhydrous. It is practically insoluble in hot ethyl acetate and petroleum (b. p. 80–90°), and only very sparingly soluble in cold water, but dissolves moderately easily in cold alcohol, readily in hot alcohol, boiling water, or cold chloroform. It undergoes no change when repeatedly crystallised from boiling water or other solvents; samples of the pure salt, which were fractionally crystallised from water, gave deposits identical in appearance, melting point, and optical properties.

The specific rotation of the  $\alpha$ -salt was determined in aqueous and in chloroform solutions, all the samples having been dried at 100°; corresponding samples are indicated by letters.

|          | Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|----------|------------|------------|-------------------|-----------------|--------------|----------------|
| I.       | 0.474      | Water      | 25 c.c.           | 200 mm.         | +2.27°       | +59.7°         |
| II.      | 0.5        | "          | "                 | "               | 2.47         | 61.7           |
| III. (a) | 0.5        | "          | "                 | "               | 2.45         | 61.2           |
| IV. (b)  | 0.5        | "          | "                 | "               | 2.44         | 61.0           |
| III. (a) | 0.5        | Chloroform | "                 | "               | 1.42         | 35.5           |
| IV. (b)  | 0.4992     | "          | "                 | "               | 1.17         | 29.4           |
|          | 0.5040     | "          | "                 | "               | 1.18         | 29.2           |
| V.       | 0.599      | "          | "                 | "               | 1.41         | 29.4           |
| VI.      | 0.5        | "          | "                 | "               | 1.33         | 33.2           |
| VII.     | 0.5034     | "          | "                 | "               | 1.21         | 30.0           |
| VIII.    | 0.4058     | "          | "                 | "               | 0.95         | 29.3           |

The results obtained for the specific rotation in aqueous solutions are practically constant; neglecting the first sample, which was possibly imperfectly purified, the mean value is  $[\alpha]_D + 61^\circ$ , which

corresponds with a molecular rotation  $[M]_D + 271^\circ$ . Since the molecular rotation of the bromocamphorsulphonic acid is  $+270^\circ$ , it might be concluded that the basic ion of this salt is optically inactive or feebly dextrorotatory, whereas, as a matter of fact, in its hydrochloride the base shows a molecular rotation of  $[M]_D - 1^\circ$ .

The first sample IIIa examined in chloroform solution gave  $[\alpha]_D + 35.5^\circ$ ; the next (IVb),  $[\alpha]_D + 29.3^\circ$ ; as this difference was too large for experimental error, the sample IVb was crystallised four or five times from water, all but about 30 per cent. separating out. The most sparingly soluble fraction, V, gave  $[\alpha]_D + 29.4^\circ$ . A fresh sample, VI, was then examined, this gave  $[\alpha]_D + 33.2^\circ$ , and in view of the previous results, particular care was taken in reading the polarimeter, so that it is certain that the rotation was not as low as  $29.3^\circ$ . Sample VI, which melted at  $222-223^\circ$ , was then crystallised six times from water and resolved into four fractions; the first (VII) and the last (VIII) melted simultaneously at  $223^\circ$ , and gave  $[\alpha]_D + 30^\circ$  and  $29.3^\circ$  respectively.

As it is hardly possible that the abnormally high results obtained with samples III and VI could be due to experimental error or to impurity, it is thought desirable to place them on record, especially as somewhat similarly abnormal observations have been previously made in the case of the partially racemic chlorocamphorsulphonates and *cis*  $\pi$ -camphanates of hydrindamine.

#### *al*-Hydrindamine d-Bromocamphorsulphonate.

The *al*-salt, the isolation of which is described above, separates from aqueous solutions in long, colourless, anhydrous needles very similar in appearance to those of the *ad*-salt, but not quite so large. From its solution in alcohol, it is deposited, on spontaneous evaporation, in massive, transparent prisms exceeding 20 mm. in length. It resembles the *ad*-salt very closely in its behaviour towards different solvents, and, like the latter, is practically insoluble in boiling ethyl acetate. The fact that the two components of the partially racemic salt may be separated in the manner already described seems, therefore, to be due to the greater solubility of the *al*-compound in a solution containing both isomerides.

When a single, large, transparent crystal of this salt is heated moderately quickly in a capillary tube, it begins to become opaque at about  $130^\circ$ , but may not melt until about  $150^\circ$ ; if, however, the crystal is crushed to a fine powder, the latter melts almost entirely at  $122-123^\circ$ , but generally solidifies again whilst in the bath and melts for a second time at  $185^\circ$ ; crystals of medium size usually melt more or less completely at about  $130^\circ$ . These observations seem to show

that the salt is polymorphous; the form deposited from aqueous solutions is apparently changed at 122—123° into a stable form melting at 185°.

Fractional crystallisation of the *al*-salt from water and dilute alcohol gave homogeneous deposits, identical in melting point and in optical properties; owing to the great difference in the appearance of the crystals of the partially racemic *a*-salt, on the one hand, and its *ad*- and *al*-components on the other, a mere inspection of the deposits from water shows whether the *ad*- or *al*-component contains any of the former or not.

The samples used for determining the specific rotation of this *al*-salt were dried at 100°, and identical preparations are indicated as before; the solvents were water and chloroform:

|       | Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|-------|------------|------------|-------------------|-----------------|--------------|----------------|
| I(a)  | 0.5        | Water      | 25 c.c.           | 200 mm.         | +2.43        | +60.7          |
| II(b) | 0.5        | "          | "                 | "               | 2.38         | 59.5           |
| III   | 0.5        | "          | "                 | "               | 2.40         | 60.0           |
| I(a)  | 0.5        | Chloroform | "                 | "               | 2.43         | 60.7           |
| II(b) | 0.4972     | "          | "                 | "               | 2.38         | 59.8           |

In aqueous solution, the average molecular rotation is, if anything, a trifle lower than that of the *ad*-salt, although the basic ion in its hydrochloride has a dextrorotation  $[M]_D + 1^\circ$ . Assuming that the *a*-salt is composed of equal quantities of the *ad*- and *al*-salts and that the specific rotations of these compounds are the same when they are in solution together as when they are separate, the molecular rotation of the partially racemic salt should be  $[M]_D + 269^\circ$ ; according to the determinations previously given (Trans., 1900, 77, 885), it is  $[M]_D + 268^\circ$ .

*The ad- and al-Salts contain Enantiomorphously Related Bases.*

The molecular rotation of the *al*- and *ad*-salts being practically identical with one another and with that of the partially racemic *a*-salt, it was necessary to prove that the latter has actually been resolved into salts of the enantiomorphously related bases; for this purpose, some *ad*-salt (about 17 grams) was decomposed with barium hydroxide; the base was distilled in steam, and the first 20 or 30 c.c. of distillate, which contained a considerable quantity of the base in suspension, were clarified by the addition of a little alcohol; on examining this solution in a 200 mm. tube, it showed a dextrorotation of  $\alpha_D + 0.75^\circ$ ; aqueous alcoholic solutions of the base obtained in a similar manner from about 17.0 grams of the *al*-salt gave a levorotation of about  $\alpha_D - 1^\circ$ .



Determinations of the specific rotations of the free bases have not been made; they are sparingly soluble in water, and the results obtained with other solvents would be of little value as regards their bearing on the present investigation.

The *hydrochloride*, obtained from the base of the *ad*-salt by neutralising with acid, separates from water in flat, transparent prisms and from cold solutions in large, very well-defined, six-sided, tabular crystals at least 10 mm. in length and 5 mm. in breadth. These crystals are very different in appearance from those of the hydrochloride of the externally compensated base, which consist of slender needles or prisms; they become opaque at about  $210^{\circ}$  and melt sharply at  $233^{\circ}$  when quickly heated, turning slightly brown; the hydrochloride of the active base is very readily soluble in water.

The *platinichlorides* of the *d*- and *l*-bases are precipitated when platinic chloride is added to solutions of the hydrochlorides. The salts are identical in appearance, both crystallising in thin, well-defined, six-sided, yellow plates. They are readily soluble in hot water and in alcohol, but only sparingly so in cold water. When heated, they behave identically, but have no definite melting point; at  $190$ — $200^{\circ}$ , according to the rate of heating, they begin to turn brown, and by the time the temperature has risen to about  $210^{\circ}$  they have become almost black.

The *picrates* were also prepared by adding a hot concentrated solution of picric acid to solutions of the *ad*- and *al*-salts respectively. The precipitates were recrystallised from hot water, from which they were deposited in yellow prisms or needles, the two preparations being identical in appearance; when rapidly heated, the two salts began to turn brown at about  $190^{\circ}$ , and decomposed completely at about  $207^{\circ}$ , their behaviour being exactly similar. The salts are only sparingly soluble in cold water.

The examination of the hydrochlorides, platinichlorides, and picrates of the bases obtained from the *ad*- and *al*-salts respectively confirm the conclusion that the bases are enantiomorphously related; there is, in fact, no other possible view, since it has been previously proved (Trans., 1900, 77, 883) that there is no structural isomeride of *dl*-hydrindamine present in the partially racemic  $\alpha$ -salt.

If further evidence is required that the bases of the *ad*- and *al*-salts are enantiomorphously related, it is afforded by the fact that they give rise to different compounds when combined with an optically active acid. The *d*-bromocamphorsulphonates themselves, the *d*-chlorocamphorsulphonates, and the *cis*- $\pi$ -camphanates prove the truth of this statement; the salts which the two bases form with Reychler's camphorsulphonic acid are also different.

*The Free Bases do not Racemise.*

The enantiomorphously related hydrindamines do not racemise when set free from their salts or when distilled in a current of steam, except, possibly, to a very minute extent; in spite of their very slight optical activity, this is easily proved beyond all doubt by the great and characteristic differences in properties between the  $\alpha$ - and  $\beta$ -partially racemic salts on the one hand, and their components on the other. When a mixture of *ad*- and a little partially racemic  $\alpha$ -salt is fractionally crystallised from water, the latter passes into the last mother liquors and is deposited from them in the characteristic opaque masses of hydrated needles, the presence of which is easily detected by mere inspection. If, however, the pure *ad*-salt is decomposed with barium hydroxide, the base distilled in steam, and again combined with the acid, the product is absolutely free from the partially racemic  $\alpha$ -salt, and does not yield a trace of the latter when systematically crystallised from water. Similar experiments with the *al*-salt also prove this, but require a more detailed description (p. 886); the examination of the hydrindamine chloro-salts in a similar manner (p. 906), and that of the *cis*- $\pi$ -camphanates\* also proves conclusively that the free bases do not racemise to any appreciable extent.

*Synthesis of the Partially Racemic  $\alpha$ -Salt.*

As the partially racemic  $\alpha$ -salt is resolved into apparently equal quantities of the *ad*- and *al*-isomerides, it was to be expected that this salt would be formed on mixing its components and crystallising the mixture from water. One gram of the pure *ad*-salt and an equal quantity of the pure *al*-isomeride were therefore dissolved together, and the solution allowed to crystallise; the deposit consisted of the characteristic opaque, felted masses of the partially racemic  $\alpha$ -salt. On evaporating the first mother liquors and separating successive fractions which seemed to be precisely similar, only one compound appeared to be present, and the last few drops gave what was obviously partially racemic  $\alpha$ -salt. When, however, the three or four fractions thus obtained were submitted to a repeated and systematic crystallisation from water, the last mother liquors gave traces of a substance which separated, together with a few minute needles, in concentrically grouped, transparent, hydrated prisms which were not those of the ordinary partially racemic  $\alpha$ -salt; the

\* The investigation of these salts is not yet concluded, but it has been ascertained that the salts of the active bases are different from the partially racemic salts already described (Trans., 1900, 77, 861; 1901, 79, 430).



nature of these two crystalline substances was not determined. The experiment showed most clearly that the partially racemic  $\beta$ -salt was not produced from the two components of the  $\alpha$ -salt, and the occurrence of the other crystalline compounds is doubtless to be explained as follows: the partially racemic salt is probably not composed of exactly equal quantities of its two components, a conclusion in accordance with the theoretical deductions as to the composition of such salts. When, therefore, equal quantities are crystallised, the one in excess will either separate alone or may form mixed crystals with some of the partially racemic  $\alpha$ -salt, thus giving rise to crystalline products of different melting points. Whether this be the true explanation or not, the fact remains that the partially racemic  $\beta$ -salt is not formed when the  $ad$ - and  $al$ -components, obtained by the resolution of the partially racemic  $\alpha$ -salt, are mixed and crystallised from water.

### *Synthesis of the Partially Racemic $\alpha$ - and $\beta$ -Salts.*

#### *Evidence of the Existence of Four Salts.*

According to the author's explanation of the formation of the two partially racemic salts from hydrindamine and  $d$ -bromocamphorsulphonic acid, there must be four distinct compounds produced when the base is neutralised with the acid. The  $ad$ - and  $al$ -salts would represent two of these compounds, one being derived from the  $d$ - and the other from the  $l$ -base. If, however, the  $ad$ -salt be decomposed, the base separated by steam distillation, and again neutralised with the acid, it should give two salts, one of which would be identical with  $ad$ , the other being a new isomeride, which may be distinguished as  $\beta d$ ; similarly, two salts should be produced from  $al$ , namely, the original  $al$ -salt, and a new isomeride,  $\beta l$ .

Now, when the experiment is actually tried, it is found that the regenerated salt obtained from  $ad$  is apparently identical with the original  $ad$ -salt; it consists of crystals indistinguishable in appearance from those of  $ad$ , and, if separated into three or four fractions by crystallisation from water, all the fractions seem to be identical and melt at practically the same temperature, the most sparingly soluble at about  $220^{\circ}$ , the most readily soluble at about  $217^{\circ}$ .

Similarly, when the  $al$ -salt is decomposed and the basic distillate neutralised with the bromo-acid, a salt is obtained which seems to be identical with the  $al$ -compound; when separated into three or four fractions by crystallisation from water, the deposits seem to be homogeneous, and all melt at the same temperature, namely, at about  $130^{\circ}$  (compare p. 879).

If, however, these regenerated salts are really mixtures, they should



behave differently from *ad* and *al*, and when mixed together and crystallised from water, they should give both the  $\alpha$ - and the  $\beta$ -partially racemic salts; experiment showed this to be the case. One gram of a fraction of the regenerated *ad*-salt deposited from the last mother liquors and 1 gram of the corresponding fraction of the regenerated *al*-salt were dissolved together in hot water and the solution cooled; the first two or three successive deposits consisted of the partially racemic  $\alpha$ -salt, but the last mother liquors deposited hydrated, transparent prisms, which were indistinguishable in appearance from the crystals of the partially racemic  $\beta$ -salt; the several deposits were systematically crystallised from water and the supposed  $\beta$ -salt obtained in a pure condition. This synthetical product was then directly compared with the ordinary partially racemic  $\beta$ -salt, and was found to be identical with it in melting point ( $130^{\circ}$  when dried at  $100^{\circ}$ ) and other properties, and repeated crystallisation failed to change it appreciably in any way.

The quantity of pure air-dried  $\beta$ -salt thus isolated was 0.37 gram, but there must also have been a considerable quantity which could not be separated from the lower fractions of the partially racemic  $\alpha$ -salt; the proportion of  $\beta$ -salt in the product obtained from *dl*-base and the bromo-acid is probably less than 15 per cent., so that the somewhat larger proportion isolated in the above experiment is due to the fact that the readily soluble fractions of the regenerated salts were used, and these were rich in the components of the  $\beta$ -salt.

The formation of the partially racemic  $\beta$ -salt from the *regenerated ad*- and *al*-salts, and its non-formation from the pure *ad*- and *al*-salts, is one of the first important pieces of evidence that the regenerated salts are really mixtures of isomerides.

That there is here no question of the conversion of the partially racemic  $\alpha$ -salt into the  $\beta$ -isomeride is absolutely certain; samples of the pure  $\alpha$ -salt have been heated on a water-bath in aqueous solution during more than 24 hours, the solution then concentrated, and the salt submitted to fractional crystallisation, but not a trace of  $\beta$ -salt could be detected.

*The Regenerated ad-Salt is a Mixture of Isomerides.*

The experiment just recorded having proved that there is some difference between the original and the regenerated *ad*-salt, a considerable quantity of the former was crystallised from water once or twice and the pure preparation then separated into several fractions; these all had the same appearance and melting point. The whole of this pure salt was then decomposed with barium hydroxide, the base steamed over, and the bromo-acid recovered from the residue by exactly precipitating

the barium with sulphuric acid; the acid was then neutralised with the aqueous distillate containing the base, the solution concentrated, and the salt obtained in three or four fractions by successive deposition. These fractions seemed to be homogeneous; they were indistinguishable in appearance, and had practically the same melting point; systematic fractional crystallisation was therefore continued until the salt (about 17 grams) had been resolved into nine fractions, the first eight of which had each been crystallised about six times, using the mother liquors from each to dissolve the next more soluble deposit; fraction IX, which consisted of the most readily soluble portions, had been recrystallised twice from a little water to free it from any impurity, and did not contain barium, sulphuric acid, or other mineral matter.

The various fractions, which still seemed to be homogeneous and identical, now differed considerably in melting point, as shown below:

| Fraction. | I.       | IV.      | VI.      | VII.     | IX.      |
|-----------|----------|----------|----------|----------|----------|
| M. p.     | 220—222° | 218—220° | 215—217° | 210—211° | 205—207° |

They also differed in specific rotation, the following results being obtained with the most sparingly soluble and most soluble portions respectively after drying the samples at 100°:

|            | Substance. | Solvent. | Volume of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|----------|---------------------|-----------------|--------------|----------------|
| Fraction I | 0.5        | water    | 25 c.c.             | 200 mm.         | +2.42°       | +60.5°         |
| „ IX       | 0.5        | „        | „                   | „               | +2.20        | +55.0          |

These two fractions were separately crystallised from water, dried, and again examined:

|            |     |       |         |         |        |        |
|------------|-----|-------|---------|---------|--------|--------|
| Fraction I | 0.5 | water | 25 c.c. | 200 mm. | +2.44° | +61.0° |
| „ IX       | 0.5 | „     | „       | „       | 2.19   | +54.7  |

Further systematic crystallisation of the fractions I—VIII raised the melting point considerably, fraction VIII then melting at 216—217°, the others at gradually increasing temperatures up to 222°. The mother liquors gave deposits which were mixed with fraction IX and the mixture crystallised from aqueous alcohol. The substance obtained in this way crystallised in large tufts of slender needles, not very unlike those of the partially racemic  $\alpha$ -salt in appearance, but anhydrous, and melting fairly definitely at 213—214°; its quantity was very small, and as there appeared to be no possibility of isolating a pure compound its further examination was deferred (this vol., 894).

These results show that the pure  $\alpha$ -salt, melting at 223°, when decomposed, as described above, and regenerated from the same base

and the same acid then contains some substance which depresses its melting point, but which cannot be separated from it except with the greatest difficulty ; this seems to show that the other substance is isomorphous with the *ad*-salt and very closely related to it, the presence of any ordinary impurity being out of the question.

In addition to the evidence of the melting point, the optical examination of fraction IX indicates the presence of a second substance of lower specific rotation than that of the *ad*-salt ; this is not a salt of the *lævo*-base, because if this were present, partially racemic  $\alpha$ - or  $\beta$ -salt would be contained in the last mother liquors and not a trace of these compounds could be found. Neither is it possible that fraction IX is a crystalline mixture of *ad*- with either of the partially racemic salts, because the crystals are anhydrous and, as has already been stated, these two salts are easily separated by crystallisation. Moreover, the presence of partially racemic  $\alpha$ -salt would not lower the specific rotation. The presence of any impurity or isomeride (*l*-acid) in the *d*-bromo-acid is also out of the question, since the acid used was that contained in the pure *ad*-salt, and the acid does not racemise under the conditions of the experiment. The only explanation of the above results, therefore, is that the regenerated salt is a mixture of two isomerides, *ad* and  $\beta d$ , which are so similar in properties that the isolation of the  $\beta d$ -form, which is present in small proportion only, is practically impossible.

*The Regenerated  $\alpha$ -Salt is a Mixture of Isomerides. Isolation of the  $\beta$ -Salt.*

Some carefully purified *al*-salt (about 5 grams) which was free from  $\alpha$ -salt was decomposed with barium hydroxide and the salt regenerated from the base, which had been separated by distillation in steam and from the *d*-bromo-acid in the residue. The solution was then concentrated and the product obtained in five crops of crystals, each of which was then crystallised about 5 times from hot water, the mother liquors from the first being used to dissolve the second, and so on ; then, on examining the several deposits, which were practically indistinguishable in appearance, and all of which crystallised in long needles just like the original *al*-salt, no appreciable difference in melting point could be detected, as they all liquefied at about 127—130°. The fifth fraction, which did not seem to crystallise so readily as the others, and which sometimes separated in an oily condition from warm solutions, was then further crystallised from water and separated into several small portions ; when some of these were allowed to crystallise slowly at the ordinary temperature, the deposits consisted of bulky, opaque masses of very slender, concentrically grouped, transparent needles, very



different in appearance from the crystals of the  $\alpha$ -salt and resembling closely the forms in which the partially racemic  $\alpha$ -salt is deposited. These masses, when warmed in contact with their mother liquor, underwent some change, the needles becoming white and opaque as if they were being dehydrated; when air-dried, however, they melted fairly sharply at  $122^\circ$ , as did a *crushed* sample of the  $\alpha$ -salt (compare p. 879).

On repeated crystallisation from water, these opaque masses yielded, as the most sparingly soluble fraction, long needles melting at about  $130^\circ$  and indistinguishable in outward properties from the crystals of the  $\alpha$ -salt, whilst the mother liquors gave again the bulky, opaque deposits. Some of the latter were collected, dried, and examined optically with the following result: 0.5 gram dissolved in chloroform, the solution made up to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha_D + 1.83^\circ$ , whence  $[\alpha]_D + 52.3^\circ$ .

Now the specific rotation of the  $\alpha$ -salt in chloroform solution is  $[\alpha]_D + 60^\circ$ , and the original sample of  $\alpha$ -salt used in this experiment had been found to have this rotation; further, when a portion of the original unregenerated salt was systematically crystallised from hot water, it did not give any of the opaque masses just referred to; it is obvious, therefore, that the regenerated salt is different from the original one. This knowledge, and certain observations made in the meantime on the resolution of the partially racemic  $\beta$ -salt, led to a repetition of the experiment, larger quantities (about 17 grams) of the pure  $\alpha$ -salt being regenerated as before and then systematically crystallised from water.

The most sparingly soluble fraction which was then obtained by crystallising 15 to 20 times from water proved to be the pure  $\alpha$ -salt, as shown by the determination of its specific rotation: 0.5 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha_D + 2.40^\circ$ , whence  $[\alpha]_D + 60^\circ$ .

From the most readily soluble portions, the bulky, opaque masses were again deposited; these were collected, dissolved in very dilute ethyl alcohol, and the solutions crystallised at the ordinary temperature. The deposits thus obtained consisted of the opaque masses, but embedded in them some rosettes of somewhat larger prisms were usually observed, and because of their greater size these crystals were slightly yellow in colour, having been deposited from a yellow solution; these rosettes were separated mechanically, the opaque masses redissolved, the deposits again examined, and the rosettes picked out, these operations being continued until the opaque masses only were obtained.

From this stage, the isolation of the new isomeride presents no very great difficulty. The yellow rosettes consist of practically pure  $\alpha$ -salt, and on recrystallisation from hot water they give the ordinary long, transparent prisms of this isomeride. The bulky, opaque masses

consist of a mixture of the  $\alpha$ - and  $\beta$ -salts, which, in presence of excess of the former, seem to separate together unchanged in some loose crystallographic union, since individual crystals become quite white and opaque when warmed with their mother liquor; when, however, the excess of the  $\alpha$ -salt has been removed mechanically in the manner described, and the opaque masses are then repeatedly crystallised from hot water, they finally yield deposits of long, transparent needles and mother liquors, which again give the opaque masses; the latter are then submitted again to crystallisation from very dilute ethyl alcohol, when rosettes of the  $\alpha$ -salt are again obtained. After this substance has been removed, repeated fractional crystallisation gives a further quantity of long needles ( $\beta$ -salt).

The needles ( $\beta$ -salt) thus obtained in very small quantities were added to the sample isolated in the first experiment and the mixture recrystallised three times from warm water; the product now seemed to be identical with the  $\alpha$ -salt; like the latter, it sintered at about  $122^{\circ}$  and melted at about  $130^{\circ}$ . Optical examination, however, showed that these needles certainly represent a new isomeride.

0.5 gram dissolved in water, the solution made up to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha_D + 1.64^{\circ}$ , whence  $[\alpha]_D + 41^{\circ}$ .

This value for the specific rotation is only about two-thirds of that of the  $\alpha$ -salt under like conditions, and is considerably lower than that of any of the salts previously examined, including the partially racemic compounds.

Three more recrystallisations from aqueous methyl alcohol lowered the specific rotation even further, the sample, when dried at  $100^{\circ}$ , then giving the following result:

0.5 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave  $\alpha_D + 1.58^{\circ}$ , whence  $[\alpha]_D + 39.5^{\circ}$ .

The further description of this isomeride is given in the following paper (p. 897).

These experiments prove beyond doubt that the salt obtained by combining the pure  $l$ -base with the pure bromo-acid consists of two isomerides, both of which crystallise in transparent needles, indistinguishable by inspection, and barely so by melting point determinations; apparently these two isomerides, which have the same solubility in cold water, crystallise together in certain definite proportions, giving deposits resembling those of the partially racemic  $\alpha$ -salt. Even knowing that the regenerated  $\alpha$ -salt is a mixture, the separation of its two components is a process of very considerable difficulty, and had it not been for the possibility of a mechanical separation of the  $\alpha$ -salt in the manner described, which again depends on a slightly coloured mother liquor, it is probable that the isolation of the pure  $\beta$ -salt would not have been successful.

The expense incurred in carrying out this and the following investigation was partly met by a Government Grant from the Royal Society, for which the author desires to express his gratitude.

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LXXXVII.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part IX. Resolution of the  $\beta$ -Modification of dl-Hydrindamine d-Bromocamphorsulphonate.*

By FREDERIC STANLEY KIPPING.

ACCORDING to the view briefly summarised in the preceding paper, the partially racemic  $\beta$ -salt, obtained from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid, should consist of a mixture of two isomerides, one derived from the *d*-, the other from the *l*-base, and these salts should be different from the *ad*- and *al*-components of the partially racemic  $\alpha$ -salt. In the expectation that the  $\beta$ -salt, like the  $\alpha$ -salt, might be resolved by crystallising it at a temperature above its transition point, experiments were carried out in hot ethyl acetate solution, and after several unsuccessful attempts, the resolution was accomplished, but only with very great difficulty.

The first product of this resolution, namely, that precipitated from the hot solution, resembles the *ad*-isomeride (p. 878) very closely in properties, and is a mixture of two salts, one identical with the *ad*-isomeride, the other doubtless identical with the  $\beta d$ -component of the regenerated *ad*-salt; it was not found possible, however, to separate completely these two isomerides, and the  $\beta d$ -modification has not yet been obtained free from the *ad*-salt.

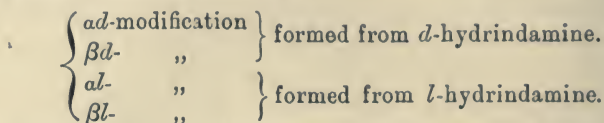
The second product of this resolution of the partially racemic  $\beta$ -salt, namely, that obtained from the ethyl acetate mother liquors, is also a mixture of two isomerides, one being identical with the *al*-component of the partially racemic  $\alpha$ -salt (p. 879), the other with the  $\beta l$ -modification contained in the regenerated *al*-salt (p. 888); these two isomerides have been separated and obtained in a pure condition.

These results seem to show that the explanation of the formation of the partially racemic  $\alpha$ - and  $\beta$ -salts originally given by the author (Trans., 1900, 77, 861) is substantially correct, and only requires modifying in one unimportant detail, namely, that the  $\beta$ -salt, instead of being composed of only two isomerides, which differ from the com-



ponents of the  $\alpha$ -salt, is really a compound formed by the crystallographic union of two new isomerides with the two components of the  $\alpha$ -salt.

The  $\beta$ -salt, therefore, consists of



This  $\beta$ -salt represents a new type of crystalline compounds which may be classed as *partially di-racemic*, since they may be regarded as formed by the crystallographic union of two partially racemic salts; as will be shown later, the *d*-bromocamphorsulphonate of *dl*-methylhydrindamine (this vol., p. 922) and the partially racemic  $\beta$ -salt of *d*-chlorocamphorsulphonic acid and *dl*-hydrindamine (this vol., p. 902) also belong to this class of interesting substances.

These partially di-racemic  $\beta$ -salts are not merely mixtures of their four components, but differ from the latter in crystalline form, and also, as a rule, in containing water of crystallisation, the components being generally anhydrous. They form well-defined, or fairly well-defined, crystals of considerable size, and under ordinary treatment, such as crystallisation from warm water, aqueous alcohol, moist ethyl acetate, and so on, they behave as if composed of only one substance.

It is obvious, therefore, that failure to resolve a compound by fractional crystallisation of its salts affords very little evidence as to whether such a compound is or is not composed of enantiomorphously related components; in the case of *dl*-hydrindamine, five different optically active acids were tried before the experiments were successful. Although these partially di-racemic salts appear to be so unchangeable, it seems possible that the relative proportions of the four components may vary within certain limits according to the temperature at which the salt is deposited and the nature of the solvent; the  $\alpha l$ - and  $\beta d$ -forms being apparently capable of forming mixed crystals, and the  $\alpha l$ - and  $\beta l$ -modifications being probably closely related to one another in crystalline form, the removal of a portion of the two  $\alpha$ -isomerides, as partially racemic  $\alpha$ -salt, might have little effect on the crystalline structure of the residual partially di-racemic salt, but would, of course, alter its specific rotation (since the  $\alpha$ - have very different specific rotatory powers from those of the  $\beta$ -modifications), and probably also its melting point. If such a variation in composition be possible, the fact would afford an explanation of the somewhat discordant results obtained in the determination of the specific rotation of the partially di-racemic hydrindamine *d*-bromo- and *d*-chlorocamphorsulphonates (Trans., 1900, 77, pp. 885, 897); the samples,

having doubtless been crystallised under slightly different conditions, were possibly not identical as regards the relative proportions of their four component isomerides. Direct observations pointing to the same conclusion have been made in the course of this work, inasmuch as samples of the partially di-racemic bromo-salt, which seemed to be free from the  $\alpha$ -isomeride, on repeated crystallisation under different conditions, have sometimes afforded a small quantity of the partially racemic  $\alpha$ -salt; long continued crystallisation, therefore, is always necessary before a sample of the  $\beta$ -salt can be regarded as pure.

That mixtures of the four isomerides, in proportions very different from those existing in the partially di-racemic salt, may enter into crystallographic union, forming an apparently homogeneous substance, is shown in this paper. The crude  $\beta d$ -salt (containing the  $ad$ -isomeride) and the pure  $\beta l$ -salt, when mixed in equal quantities and crystallised, give a hydrated compound which is indistinguishable from the ordinary partially di-racemic  $\beta$ -salt by inspection, but which, nevertheless, differs from it in melting point and specific rotation.

#### EXPERIMENTAL.

The separation of the components of the partially racemic  $\beta$ -salt of hydrindamine and  $d$ -bromocamphorsulphonic acid is a far more troublesome process than the resolution of the  $\alpha$ -salt, partly because of the smaller quantities of this isomeride which are available, but principally because of its more complex character; as shown below, it consists of four components.

The  $\beta$ -salt, freed from the  $\alpha$ -isomeride by repeated crystallisation from water and dilute alcohol, is dried in the air and dissolved in a small quantity of ethyl acetate, in which the hydrated crystals are readily soluble. The solution is then placed in a beaker covered with a clock-glass, and left on the water-bath for some hours, when the syrupy residue thus obtained usually begins to deposit minute crystals; a little more dry ethyl acetate is then added, and the heating continued, whereupon a small proportion of the salt is slowly deposited in silky needles; this deposit ( $a$ ) is rapidly separated from the hot solution and washed thoroughly with boiling ethyl acetate, in which it is only very sparingly soluble.

If the operation has been successful, this precipitate ( $a$ ), on recrystallisation from water, will give long, slender needles, and will be practically free from any partially racemic  $\beta$ -salt; if, however, precipitation has been carried too far, the substance deposited from the aqueous solution may consist almost entirely of unchanged  $\beta$ -salt, which separates in rosettes of hydrated prisms.

The ethyl acetate filtrate and washings from the original deposits,

when concentrated on the water-bath, may or may not give a second deposit of silky needles, according to the manner in which the first operation has been conducted; if no precipitate forms, the addition of light petroleum (b. p. 80—90°) and further heating may cause a second separation from the hot solution; the petroleum, however, must be added very cautiously, otherwise the solution separates into two layers and the lower one then solidifies to a mass of unresolved salt. When it is found that no further resolution occurs on continued heating, the ethyl acetate solution is mixed with a few drops of water and left at the ordinary temperature until most of the solvent has evaporated; the deposit, which consists of the hydrated, partially racemic  $\beta$ -salt, is separated and submitted again to the original treatment; the filtrate is evaporated to dryness, the residue dissolved in a considerable quantity of cold water, and after some time the cold solution (*b*) is filtered from traces of resinous matter and concentrated.

The original  $\beta$ -salt is thus resolved by repeated treatment into the substance (*a*) melting at about 215°, and the substance or substances in the aqueous solution (*b*).

#### *Examination of the Precipitate (a).*

The substance which separates from the hot ethyl acetate solution of the  $\beta$ -salt crystallises from water in long, silky needles, but from hot saturated solutions it is deposited as an oil. When freed from partially racemic salt by one or two crystallisations from water, it melts, not quite sharply, between 213° and 216°, generally at about 215°, and is indistinguishable in outward properties from the *ad*-salt (p. 878).

As this preparation was conceivably one of the two salts of which the partially racemic  $\beta$ -compound was supposed to consist, a sample was dried at 100° and examined optically, with the following results:

| Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|-----------------|--------------|----------------|
| 0.5010     | Water      | 25 c.c.           | 200 mm.         | +2.33°       | +58.25°        |
| 0.4078     | Chloroform | „                 | „               | +0.98        | +30.0          |

These values agree very closely with those of the *ad*-salt, namely, +61° in aqueous and +30° in chloroform solution; further, the melting point of this new substance is not very different from that of the *ad*-salt.

Now the sample of  $\beta$ -salt from which this substance had been prepared was repeatedly crystallised before submitting it to resolution, and it seemed quite impossible that the above substance could be



derived from some partially racemic  $\alpha$ -salt which had escaped detection; nevertheless, a fresh sample of  $\beta$ -salt was purified even more carefully than before, and this preparation was then resolved. The deposit ( $\alpha$ ), as before, crystallised from water in long needles melting at  $215-216^\circ$  fairly sharply, and when mixed with  $\alpha d$ -salt it gave a mixture melting at  $218^\circ$ . Its specific rotation was determined with the following results:

| Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|-----------------|--------------|----------------|
| 0.5436     | Water      | 25 c.c.           | 200 mm.         | $2.44^\circ$ | $56.3^\circ$   |
| 0.5436     | Chloroform | „                 | „               | 1.25         | 28.7           |

A third sample, prepared from a different specimen of the  $\beta$ -salt, also melted at  $214-216^\circ$ , and its melting point did not change appreciably after three crystallisations from water; its specific rotation was determined in aqueous solution and found to be  $[\alpha]_D +58.7^\circ$ , a value which agreed closely with that of the first preparation.

Now from the results of the experiments with the regenerated  $\alpha d$ -salt, the component of the  $\beta$ -salt, namely,  $\beta d$ , has a specific rotation less than  $[\alpha]_D +50^\circ$  in aqueous solution; it seemed, therefore, that the substance actually obtained from the  $\beta$ -salt could not consist of the pure  $\beta d$ -modification.

A considerable quantity of the mixture of the three different preparations obtained from the partially racemic  $\beta$ -salt was next submitted to a systematic fractional crystallisation from water, and thus resolved into eight portions, each of which had been crystallised 8-10 times; the most sparingly soluble (fraction I) and the most readily soluble (fraction VIII) were then examined; they melted at  $217-219^\circ$  and at  $208-212^\circ$  respectively, and had the following specific rotations in aqueous solution:

|                  | Substance. | Vol. of solution. | Length of tube. | $\alpha_D$ .  | $[\alpha]_D$ . |
|------------------|------------|-------------------|-----------------|---------------|----------------|
| Fraction I ..... | 0.502      | 25 c.c.           | 200 mm.         | $+2.42^\circ$ | $+59.9^\circ$  |
| Fraction VIII... | 0.4955     | „                 | „               | 2.18          | 55.0           |

It thus appeared that the product from the  $\beta$ -salt is not a single substance; fraction I seemed to be identical with the  $\alpha d$ -salt, fraction VIII with the mixture of  $\alpha d$ - and  $\beta d$ -salts obtained from the regenerated  $\alpha d$ -isomeride (p. 884); as, however, fraction VIII might conceivably have contained traces of the partially racemic  $\beta$ -salt, it was thrice crystallised from water, and again examined optically; its specific rotation in aqueous solution was then  $[\alpha]_D +56.2^\circ$ .

Fractional crystallisation was therefore continued, aqueous methyl alcohol being used instead of water, and after many operations the melting point of the most sparingly soluble portion rose to  $222-223^\circ$ ,

which is identical with that of the *ad*-salt; its specific rotation in aqueous solution was also identical with that of this isomeride.

The most readily soluble portions now melted almost sharply at 213—214°, and, when examined polarimetrically, gave the following values :

| Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|-----------------|--------------|----------------|
| 0.5        | Water      | 25 c.c.           | 200 mm.         | +2.23°       | +55.75°        |
| 0.5        | Chloroform | ,,                | ,,              | 1.25         | 31.0           |

These results prove that the precipitate (*a*) obtained in the resolution of the pure partially racemic  $\beta$ -salt is a mixture of isomerides, one of which is identical with the *ad*-isomeride, the other being doubtless identical with the  $\beta d$ -modification, the existence of which has already been shown to be probable.

Many attempts have been made to obtain the  $\beta d$ -isomeride in a pure condition; the most readily soluble portions of the salt referred to above were mixed with the most readily soluble fractions of the regenerated *ad*-salt (p. 885), and the mixture systematically crystallised from water and dilute alcohol until all the more sparingly soluble substances had been separated. About 1.5 grams remained, representing the most soluble portion obtained from about 50 grams of salt; this melted at 200—203°, and had a specific rotation  $[\alpha]_D +51^\circ$  in aqueous solution. It was crystallised twice from water, the more sparingly soluble portions (about half) being rejected; the mother liquors were then evaporated and the deposit crystallised from ethyl acetate and a little methyl alcohol. The substance finally obtained melted at 207—208°, and had a specific rotation of  $[\alpha]_D +49.2^\circ$  in aqueous solution; this sample represents the most concentrated form of the  $\beta d$ -isomeride which has yet been prepared.

It is very doubtful whether it would be possible to obtain the  $\beta d$ -salt quite free from its *ad*-isomeride; the two substances are obviously very similar in properties and form mixed crystals.

The impure  $\beta d$ -salt of specific rotation  $[\alpha]_D +49.2^\circ$  differs from the *ad*-isomeride principally in the manner in which it crystallises from cold water and from aqueous alcohol; from the former, it is deposited in large, opaque tufts of concentrically grouped, slender needles, from the latter in bunches of ill-defined prisms, whereas the *ad*-salt gives a transparent deposit of separately-formed, coarse needles and of massive, well-defined prisms respectively.

Although these differences may appear to be unimportant, there is not the least doubt as to the existence of the  $\beta d$ -isomeride; the very fact that there is so much difficulty in separating the two components of the deposit (*a*) is almost conclusive evidence that they are very closely

related and that the lower melting point and specific rotation of the more soluble portions of this substance are not due to the presence of any ordinary impurity. If these results stood alone, they might possibly still leave an impression of doubt; fortunately, they are confirmed in every respect by the experiments described later, especially by the results of the investigation of the corresponding salts of *d*-chloro-camphorsulphonic acid, as in this case the isolation of the pure  $\beta d$ -isoméride was accomplished.

*Examination of the Aqueous Solution (b).*

The aqueous solution (b) obtained in treating the products of the resolution of the  $\beta$ -salt (p. 892), when crystallised slowly at the ordinary temperature, may give, first, either a deposit of partially racemic  $\beta$ -salt, in the form of yellow prisms or nodules, or white, bulky masses consisting of minute, concentrically grouped needles, which at first were thought to consist of partially racemic  $\alpha$ -salt, so closely do they resemble the deposits of the latter. If the partially racemic  $\beta$ -salt separates first, crystallisation is continued until white specks appear, and the solution is then decanted and further evaporated. The bulky, white masses thus obtained melt somewhat indefinitely at about  $122^{\circ}$ , and when recrystallised from water are deposited apparently unchanged, except that their mother liquors often afford small quantities of the  $\beta$ -salt; on repeated fractional crystallisation, however, the deposits become more and more definite, and after about ten operations a relatively very small quantity of an apparently pure product is obtained.

This substance crystallised from water in long needles melting at about  $130^{\circ}$ ; when separated into two fractions by crystallisation from water, the two fractions seemed to be homogeneous and identical. They were dried at  $100^{\circ}$  and examined optically in aqueous and in chloroform solution, with the following results:—

|            | Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ .   | $[\alpha]_D$ . |
|------------|------------|------------|-------------------|-----------------|----------------|----------------|
| Fraction I | 0.5724     | Water      | 25 c.c.           | 200 mm.         | $1.88^{\circ}$ | $41.1^{\circ}$ |
| „ II       | 0.4570     | „          | „                 | „               | $1.63$         | $44.6$         |
| „ I        | 0.5724     | Chloroform | „                 | „               | $1.85$         | $40.4$         |
| „ II       | 0.4570     | „          | „                 | „               | $1.54$         | $42.1$         |

These values are very different from those given by the  $\alpha$ -salt under corresponding conditions, and the optical examination seems to show that this new substance is identical with the  $\beta$ *l*-isomeride obtained from the regenerated  $\alpha$ -salt (p. 888), but is not quite pure; on further investigation, these conclusions were fully confirmed and this substance is therefore referred to as the  $\beta$ *l*-salt.



The various aqueous filtrates resulting from the crystallisation of the  $\beta$ l-salt give, when evaporated at the ordinary temperature, deposits which generally contain three compounds, namely, the partially racemic  $\beta$ -salt, the opaque, white masses, and small rosettes of prisms; the latter crystals being of some size are distinctly yellow, and can thus be picked out from the deposits; when dissolved in hot water, they separate again, on cooling, in long needles which melt at about  $130^{\circ}$  and appear to be identical with the crystals of the  $\beta$ l-salt; if, however, they are mixed with some  $\beta$ l-salt, the mixture, when dissolved in hot water, gives an oily product, whereas the  $\beta$ l-isomeride separates in crystals even on the water-bath. When crystallised slowly, moreover, the solution of this mixture gives the opaque, white masses.

The rosettes of yellow prisms, therefore, are different from the crystals of the  $\beta$ l-isomeride, and this conclusion is confirmed by the results of polarimetric examination obtained with two different samples dried at  $100^{\circ}$ .

| Substance. | Solvent. | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|----------|-------------------|-----------------|--------------|----------------|
| 0.502      | Water    | 25 c.c.           | 200 mm.         | +2.36°       | +58.7°         |
| 0.418      | "        | "                 | "               | 1.94         | 58.0           |

As the specific rotation of the  $\alpha$ l-salt in aqueous solution is  $[\alpha]_D + 60^{\circ}$ , and as these samples (which, however, were not very carefully purified) have all the other properties of the  $\alpha$ l-isomeride, there is no doubt that the latter is a component of the partially racemic  $\beta$ -salt.

The isolation of the  $\beta$ l-salt, which in any case is very troublesome, is best accomplished by the method previously described in the case of the regenerated  $\alpha$ l-salt (p. 887); after repeatedly crystallising from cold dilute methyl alcohol (not fractionally) and picking out every time any crystals of the  $\alpha$ l- or of the partially racemic  $\beta$ -salt which can be observed, the white, opaque masses are fractionally crystallised from warm water until the most sparingly soluble portion separates in distinct needles of some size. The mother liquors, again, give the white, opaque masses, which, having been separated from some  $\beta$ l-salt, when recrystallised from aqueous methyl alcohol furnish the rosettes of the  $\alpha$ l-isomeride; these are removed and the operations continued.

In this way, the substance in the aqueous solution (b) is finally separated into  $\alpha$ l-salt, crude  $\beta$ l-salt, and the partially racemic  $\beta$ -salt.

There is another method which sometimes gives the  $\beta$ l-salt in small quantities, but which is very uncertain; this is, to evaporate on the water-bath the ethyl acetate filtrate from the original deposit (a), when the oily residue gradually solidifies to a solid mass; if this is now repeatedly extracted with boiling ethyl acetate, the residue, when dissolved in water, gives the white, opaque masses of the mixture of  $\alpha$ l- and  $\beta$ l-salts, the former being generally present in relatively

small proportion; from these deposits, the  $\beta l$ -salt is isolated by the method already described. The curious fact is here observed that, whereas the first deposit from the hot ethyl acetate solution of the partially racemic salt consists of the  $\alpha d$ - and  $\beta d$ -isomerides, the most sparingly soluble portion of the residue just referred to is a mixture of the  $\alpha l$ - and  $\beta l$ -salts; this is doubtless because all the four components  $\alpha d$ ,  $\alpha l$ ,  $\beta d$ ,  $\beta l$ , are practically insoluble in boiling ethyl acetate when separated from the others, but are soluble in presence of the corresponding isomeride. In resolving the  $\beta$ -salt, it often happens that, although the original precipitate may appear to be a satisfactory resolution product and melt at a temperature far above the melting point of the partially racemic salt, yet when crystallised from water it gives a deposit consisting almost entirely of the latter; in such cases, therefore, the precipitate contains all the four isomerides.

*Final Products of the Resolution of the  $\beta$ -Salt.*

The following are the various products of the resolution of the partially racemic  $\beta$ -salt:

- (1) Pure  $\alpha d$ -salt; m. p. 222—223°;  $[\alpha]_D +59.9^\circ$  in water.
- (2) Impure  $\beta d$ -salt; m. p. 207—208°; „ +49.2 „
- (3) Pure  $\alpha l$ -salt; m. p. indefinite (130°); „ +59.0 „
- (4) Pure  $\beta l$ -salt; m. p. „ (130°); „ +39.4 „
- (5) Mixtures of the  $\alpha d$ - and  $\beta d$ -salts in various proportions.

The quantities of (3) and (4) are approximately the same, and the sum of the weights of (1), (2), and (5) is approximately equal to that of the weights of (3) and (4); it may be concluded, therefore, that the partially racemic  $\beta$ -salt is composed of approximately equal quantities of the four isomerides, but it is impossible to make more than a rough estimate.

*$\beta l$ -Hydrindamine Bromocamphorsulphonate.*

Various samples of the  $\beta l$ -salt obtained in the resolution of the partially racemic  $\beta$ -salt gave, when examined optically in aqueous solution,  $[\alpha]_D +40.4^\circ$ ,  $+44.6^\circ$ , and  $+41.8^\circ$ , whereas samples of the  $\beta l$ -salt, isolated from the regenerated  $\alpha l$ -modification (p. 888), gave  $+41^\circ$  and  $+39.5^\circ$  respectively; all these preparations crystallised in long needles, and were seemingly pure, but, nevertheless, most of them contained small quantities of the  $\alpha l$ -isomeride, of which  $[\alpha]_D = +60^\circ$ .

A considerable quantity of this crude  $\beta l$ -salt having been prepared from the partially racemic  $\beta$ -compound, the whole was crystallised four times from water and aqueous methyl alcohol alternately, and the most sparingly soluble portion separated and dried at 100° (sample I).

Its specific rotation was then determined in chloroform and in aqueous solutions :

| Sample | Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|--------|------------|------------|-------------------|-----------------|--------------|----------------|
| I      | 0.5        | Chloroform | 25 c.c.           | 200 mm.         | 1.47°        | 36.7°          |
| „      | II         | 0.5        | „                 | „               | 1.46         | 36.5           |
| „      | III        | 0.5        | „                 | „               | 1.47         | 36.7           |
| „      | I          | 0.5        | Water             | „               | 1.58         | 39.4           |

The two samples (II and III) were obtained in later preparations, and purified in a similar manner.

Further crystallisation failed to change the optical or other properties of this isomeride in any way, and the final value (+39.4°) obtained in aqueous solution agrees very closely with that of the pure sample of  $\beta$ l-salt isolated from the regenerated  $\alpha$ l-modification ; as the small quantity of the  $\alpha$ l-isomeride present in the crude  $\beta$ l-salt becomes removed, the crystals of the latter gradually change from tufts of minute needles to distinct, lustrous prisms, and after some experience it is easy to tell by mere inspection when the  $\beta$ l-salt is free from its isomeride.

That the pure substance is identical with the  $\beta$ l-component of the regenerated  $\alpha$ l-salt is proved by the identity in optical properties and in all other respects ; samples from the two sources, when mixed and crystallised, behaved like a single substance.

Although several analyses of the partially racemic  $\beta$ -salt had been previously made (*loc. cit.*), and there could consequently be little doubt as to the composition of this  $\beta$ l-salt, a halogen determination was made with a pure sample dried at 100° :

0.306 gave 0.1285 AgBr. Br = 17.9.

$C_{10}H_{14}OBr \cdot SO_3H, C_9H_{11}N$  requires Br = 18.0 per cent.

This  $\beta$ l-salt seems to be more sparingly soluble in warm water than the  $\alpha$ l-isomeride, but at the ordinary temperature their solubilities are the same, as was found experimentally ; it separates from moderately concentrated warm solutions in long prisms or needles, from very concentrated hot solutions in felted masses which seem to be crystallographically different from the needles ; even when its solutions are evaporated on the water-bath, the pure  $\beta$ l-salt separates in crystals, whereas the  $\alpha$ l-isomeride under these conditions is often deposited as an oil. The  $\beta$ l-salt crystallises from aqueous methyl alcohol in fairly large, semi-transparent prisms, less well-defined than those of the  $\alpha$ l-isomeride, which, however, it resembles very closely in most other respects. Like the latter, it does not melt definitely, a fact which adds to the difficulty of isolating a pure preparation ; many melting point determinations have been made, but the behaviour of the salt



varies so much with the size of the crystals and with the rate of heating that concordant results are seldom obtained. The finely powdered salt sometimes melts almost completely at about  $122^{\circ}$ , but sometimes shows very little change until about  $233^{\circ}$ ; single crystals of moderate size sometimes melt almost entirely and fairly sharply at  $128-130^{\circ}$ , sometimes only partially even at  $138^{\circ}$ ; even if fusion, partial or complete, occurs at these relatively low temperatures, the salt generally solidifies again and melts for a second time at about  $233^{\circ}$ , decomposing slightly. It may be inferred that this behaviour is due to dimorphism; the form obtained from aqueous solutions has probably a melting or transition point of about  $122^{\circ}$ , at which temperature it passes more or less completely and rapidly, according to the conditions of the experiment, into a modification melting at a higher temperature; whether the second melting point or decomposition point ( $233^{\circ}$ ), which is fairly constant, is that of this second crystallographic modification or that of some compound of acid and salt has not been determined.

*Synthesis of the partially Racemic  $\beta$ -salt (m. p.  $130^{\circ}$ ).*

The first results of the experiments on the resolution of the  $\beta$ -salt seemed to show that this substance was composed of *two* salts, namely, the component melting at about  $215-216^{\circ}$ , obtained from the deposit (a) (p. 892), and the component crystallising in tufts of needles melting at about  $122^{\circ}$  obtained from the aqueous solution (b) (p. 895); before it was known that each of these components is a mixture of isomerides, it seemed desirable to ascertain whether or not they were identical with the components of the partially racemic  $\alpha$ -salt which respectively they resembled very closely. The best way of doing this seemed to be to mix the two  $\beta$ -products in equal quantities and crystallise the mixture from water; this experiment was therefore made.

The sample of the less fusible component which was used had been crystallised only once or twice from water to free it from partially racemic  $\beta$ -salt, and probably consisted, therefore, of the isomeric *ad*- and *bd*-salts in practically the same proportions as they occur in the partially racemic  $\beta$ -component; the sample of the more fusible component, however, had been fractionally crystallised from water, and probably contained a larger proportion of the  $\beta$ -isomeride than the original mixture. Nevertheless, on crystallising the mixed salts from water, a substance was deposited in transparent, well-defined, hydrated prisms which were indistinguishable in appearance from the crystals of the ordinary partially racemic  $\beta$ -salt, and which, when dried, had the melting point of the latter. Crystallisation of this synthetical product failed to reveal the presence of any of the partially racemic  $\alpha$ -salt.

This experiment proves that the ordinary partially racemic  $\beta$ -salt is really a mixture of four isomerides, and that the *ad*- and *al*-components which are obtained from it are not derived from the partially racemic  $\alpha$ -salt present as impurity.

*Synthesis of a New partially Racemic  $\beta$ -Salt.*

Having found that the two components used in the preceding experiment were both mixtures of isomerides, and that the ordinary  $\beta$ -salt consists of four substances, it seemed interesting to ascertain the result of mixing the pure  $\beta$ l-salt with the (impure)  $\beta$ d-isomeride.

For this purpose, a sample of pure  $\beta$ l-salt having a specific rotation of  $[\alpha]_D + 36.5^\circ$  in chloroform and  $[\alpha]_D + 39.4^\circ$  in aqueous solution was mixed with an equal quantity of a sample of impure  $\beta$ d-salt having the values  $[\alpha]_D + 31^\circ$  and  $[\alpha]_D + 55.7^\circ$  under corresponding conditions.

The specific rotation of the mixture was then determined, with the following results :

| Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|-----------------|--------------|----------------|
| 0.5        | Chloroform | 25 c.c.           | 200 mm.         | +1.64°       | +41°           |
| 0.5        | Water      | „                 | „               | 1.93         | 48.5           |

On crystallising the mixture from water, a salt was deposited in rosettes of well-defined, transparent prisms, indistinguishable by inspection from the crystals of the ordinary partially racemic  $\beta$ -salt; these prisms, moreover, contained water of crystallisation, an air-dried sample losing 2.6 per cent. of water when heated at  $100^\circ$  during 7 hours, and 3.09 per cent. after heating during 13 hours; the ordinary  $\beta$ -salt contains 2.7 per cent. of water.

Obviously, however, this substance cannot be identical with the ordinary partially racemic  $\beta$ -salt, and as a matter of fact it differs from the latter in melting point; when previously dried at  $100^\circ$ , instead of melting at  $130^\circ$  (the melting point of ordinary  $\beta$ -salt), it fuses fairly sharply at  $158$ – $160^\circ$ , probably undergoing some crystallographic change at lower temperatures, since it seems to melt partially at about  $140^\circ$  and then solidify again.

A consideration of the optical properties of this salt in different solvents affords insufficient evidence that it is different from the ordinary partially racemic  $\beta$ -salt. Calculating from the values of its components, its specific rotation in chloroform should be  $[\alpha]_D + 33.7^\circ$  and in water  $[\alpha]_D + 47.5^\circ$ , those actually found being  $[\alpha]_D + 41^\circ$  and  $+48.5^\circ$  respectively; in chloroform, therefore, the observed is very different from the calculated value, whereas in aqueous solution the two values are practically the same, showing that in the latter case the

presence of the one isomeride does not seem to change appreciably the specific rotation of the other.

Now the specific rotation of the ordinary partially racemic  $\beta$ -salt was previously given as  $+41.5^\circ$  in chloroform (one determination only), and from  $+48.3^\circ$  to  $+54.3^\circ$  in water; taking the lowest of these values in aqueous solution, the results agreed very closely with those obtained with the synthetical salt.

During the present investigation, a specimen of the ordinary partially racemic  $\beta$ -salt was obtained by crystallisation from aqueous alcohol in large, beautifully defined, flat prisms, all of which were obviously identical; as this sample seemed to represent a perfectly definite compound, it was dried in the air and examined optically, with the following results:

| Substance. | Solvent.   | Vol. of solution. | Length of tube. | $\alpha_D$ .  | $[\alpha]_D$ . |
|------------|------------|-------------------|-----------------|---------------|----------------|
| 0.5        | Chloroform | 25 c.c.           | 200 mm.         | $+1.82^\circ$ | $+45.5^\circ$  |
| 0.5        | Water      | „                 | „               | 2.16          | 54.0           |

Calculating for the anhydrous substance, the values would be

$$\text{chloroform: } [\alpha]_D + 46.8^\circ, \quad \text{water: } [\alpha]_D + 55.5^\circ,$$

which are higher in both cases than any previously obtained.

From the results of these experiments, it would seem, therefore, that the four isomerides of the ordinary partially racemic  $\beta$ -salt may crystallise together in different proportions, giving products which are apparently homogeneous, and which have all the ordinary characteristics of a pure single substance; a change in the solvent or in the temperature at which crystallisation occurs probably causes a slight alteration in the proportions of the four components of the  $\beta$ -salt without appreciably altering the crystalline form, so that on fractionally crystallising under ordinary conditions, a number of slightly different substances may be obtained. In any case, on crystallising the original salt, obtained from *dl*-hydrindamine and *d*-bromocamphor-sulphonic acid, the whole of the  $\beta d$ - and  $\beta l$ -components remain in the deposits of partially racemic  $\beta$ -salt, since the two products of the resolution of the  $\alpha$ -salt are homogeneous, and consist of the pure *ad*- and *al*-isomerides respectively.

That the partially racemic  $\alpha$ -salt is free from the  $\beta d$ - and  $\beta l$ -isomerides might be inferred from a consideration of the specific rotation of the salt itself and those of its components, the values in 2 per cent. aqueous solution being as follows:

$$\alpha\text{-Salt: } [\alpha]_D + 60.8^\circ; \quad ad\text{-salt: } [\alpha]_D + 61^\circ; \quad al\text{-salt: } [\alpha]_D + 60^\circ.$$

Taking the values in 2 per cent. aqueous solution, the average for the partially racemic  $\beta$ -salt is about  $[\alpha]_D + 51.0^\circ$ ; those of its components are as follows: *ad*-salt,  $+61^\circ$ ; *al*-salt,  $+60^\circ$ ;  $\beta d$ -salt



(impure),  $+50^\circ$ ;  $\beta$ *l*-salt,  $+39^\circ$ . Assuming that the ordinary partially racemic  $\beta$ -salt contains approximately equal quantities of all four components, its calculated specific rotation would be  $[\alpha]_D +52.5^\circ$ .

It is an interesting question whether the *ad*- and *al*-isomerides and the  $\beta$ *d*- and  $\beta$ *l*-forms are actually produced in equal quantities on combining the *dl*-base with the acid, or whether a larger proportion of, say, the *ad*-salt is formed from *d*-base than of *al*-salt from the *l*-base; from theoretical considerations, equality is, perhaps, to be expected.

A comparison of the properties of the four isomeric hydrindamine bromocamphorsulphonates, described in this and in the preceding paper, with those of the corresponding *d*-chlorocamphorsulphonates (see below) and a discussion of their isomerism form the subject of a later communication (p. 937).

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LXXXVIII.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part X. The Four Isomeric Hydrindamine d-Chlorocamphorsulphonates*  
 $\text{NR}_1\text{R}_2\text{H}_3$ .

By FREDERIC STANLEY KIPPING.

THE further investigation of the partially racemic  $\alpha$ - and  $\beta$ -salts derived from *dl*-hydrindamine and *d*-chlorocamphorsulphonic acid (Kipping, *Trans.*, 1900, 77, 889) was a natural consequence of the results described in the preceding papers, and it was expected, from the close relationship between corresponding salts of the two acids, that the methods used for the resolution of the bromo-compounds would be equally successful in the case of the chloro-derivatives; these expectations, however, were not realised; it was not found possible to resolve either of the partially racemic salts of the chloro-acid by crystallising from boiling ethyl acetate, with or without the addition of light petroleum.

Fortunately, an alternative method was available for the isolation of the four isomerides, the existence of which had been premised, namely, to combine the optically active bases obtained from the bromo-salts with the chloro-acid, and then to submit the products to fractional crystallisation; the results of these experiments may be summarised as follows.

*d*-Hydrindamine, prepared from the pure *ad*-component of the

partially racemic bromo-salt, combines with *d*-chlorocamphorsulphonic acid, giving two isomeric salts in very unequal quantities.

The principal product, which corresponds with the *ad*-bromo-salt, and which is therefore distinguished as the  $\alpha$ -isomeride, is easily obtained in a pure condition. It separates from water in well-defined, compact, hydrated crystals, melts at 208—209° when dehydrated, and has a specific rotation  $[\alpha]_D + 46^\circ$  in aqueous and  $[\alpha]_D + 15.5^\circ$  in chloroform solution. It is very different in ordinary properties from the corresponding *ad*-bromo-salt, and also from all the other three isomeric chloro-salts.

The second product, which corresponds with the  $\beta d$ -bromo-salt, is formed in relatively very small quantities, but can nevertheless be isolated in what seems to be a pure condition. This  $\beta d$ -isomeride crystallises from water in long, hydrated needles and melts at 202—203° when dehydrated; its specific rotation is  $[\alpha]_D + 59^\circ$  in aqueous and  $[\alpha]_D + 50.0^\circ$  in chloroform solution.

The great difference in outward characters between these isomerides is very noteworthy considering the great similarity which seems to exist between the corresponding *ad*- and  $\beta d$ -forms of the bromocamphorsulphonate; it is also interesting to note that in spite of these differences the isolation of the  $\beta d$ -isomeride is exceedingly troublesome, this modification retaining small quantities of the *ad*-compound with great tenacity.

That these two chloro-salts are really produced from identical components was proved by decomposing the pure *ad*-form and regenerating the salt from the same acid and the same base; the product consists of a mixture of the *ad*- and  $\beta d$ -isomerides.

As the  $\beta d$ -chloro-salt has a much higher specific rotation than the *ad*-isomeride, it is obvious that its formation cannot be attributed to racemisation of the chloro-acid.

*l*-Hydrindamine, prepared from the pure *al*-modification of the bromo-salt, also combines with *d*-chlorocamphorsulphonic acid, giving rise to a mixture of very unequal quantities of two isomerides.

The principal product, the *al*-modification, corresponding with the *al*-bromo-salt, separates from water in long, anhydrous needles, indistinguishable by inspection from those of the *al*-bromo-compound; it melts at 118—119° and has a specific rotation  $[\alpha]_D + 44^\circ$  in aqueous, and  $[\alpha]_D + 45.5^\circ$  in chloroform solution.

The subsidiary product, namely, the  $\beta l$ -isomeride, is formed in relatively very small quantities, and its separation from the *al*-salt is a most troublesome operation; nevertheless, it can be isolated in a pure condition, and then crystallises from water in long, anhydrous needles melting very indefinitely at about 140°. Its specific rotation is  $[\alpha]_D + 57.5^\circ$  in aqueous and  $[\alpha]_D + 60.5^\circ$  in chloroform solution. This

$\beta$ l-chloro-salt closely resembles the corresponding bromo-isomeride in nearly all respects, and like the latter seems to be dimorphous.

The pure *al*-form of the chloro-acid, when decomposed and regenerated from the same acid and the same base, gives rise to both the *al*- and  $\beta$ l-modifications, so that the isomerism of the two compounds is of the same type as that of the *ad*- and  $\beta$ d-salts. Here, again, since the subsidiary product has a higher specific rotation than its isomeride, its formation cannot be attributed to racemisation of the chloro-acid.

The isolation of these four isomeric hydrindamine chlorocamphorsulphonates affords strong support to the author's views as to the nature of the isomeric partially racemic salts, but a discussion of their properties from this standpoint is postponed until the isomeric derivatives of methylhydrindamine have been described (p. 918).

#### EXPERIMENTAL.

##### *Attempts to Resolve the partially Racemic $\alpha$ - and $\beta$ -Salts.*

It has already been mentioned that the resolution of the partially racemic hydrindamine chlorocamphorsulphonates (Trans., 1900, *loc. cit.*) has not yet been accomplished, and the difference in behaviour between these salts and those of the bromo-acid is certainly noteworthy.

The partially racemic  $\alpha$ -salt was dissolved in a very small quantity of alcohol, the solution evaporated to a syrup, and hot ethyl acetate added, together, in some cases, with a slight amount of light petroleum (b. p. 80—90°); on allowing the solution to simmer on the water-bath, very slender needles were slowly deposited, just as in the case of the bromo-salt, and it seemed that a partial resolution had occurred; when, however, this precipitate was separated and dissolved in water, the solution gave deposits of the bulky, opaque masses of the partially racemic  $\alpha$ -salt. Fractional crystallisation of the original deposit from boiling ethyl acetate was also tried, the operations being continued until only a very small quantity of salt remained, but even this preparation seemed to consist of approximately equal quantities of the *ad*- and *al*-components, as when crystallised from water it gave the hydrated partially racemic salt.

The partially racemic  $\beta$ -salt was examined in a somewhat similar manner, but it could not be made to crystallise from the hot solutions, and, on cooling, crystals of the original  $\beta$ -salt were slowly deposited.

##### *Formation and Separation of the $\alpha$ d- and $\beta$ d-Isomerides.*

The pure *ad*-modification of hydrindamine bromocamphorsulphonate (this vol., p. 878) was decomposed with barium hydroxide solution, the



base distilled in steam, and the distillate neutralised with *d*-chloro-camphorsulphonic acid, prepared from the carefully purified ammonium salt (Kipping and Pope, Trans., 1895, 67, 354); after having been concentrated, the solution, on cooling, deposited a large quantity of salt in long, opaque bundles or bands of small prisms; this salt was removed, the solution concentrated, and the first and successive deposits, repeatedly and systematically crystallised from water and aqueous alcohol.

The salt was thus separated into seven fractions, each of which, excepting the last, had been crystallised about six times, the mother liquors from the first (fraction I) being used to dissolve the next, and so on; fraction VII was obtained by evaporating the final mother liquors to a small bulk and then separating the whole of the deposit from the cold solution.

All the fractions thus obtained seemed to be identical, and consisted of broad, opaque bands of characteristic appearance; melting point determinations indicated the presence of water of crystallisation, the several fractions partly liquefying at about 140°, then gradually solidifying and melting again at 203—208°.

When dried at 100°, fraction I melted sharply at 208—209°; fraction VII sintered at 203—204°, and melted at 206—207°.

The specific rotations \* of these two fractions (dried at 100°) were determined in chloroform and in aqueous solutions, with the following results:

|            | Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|------------|-------------------|--------------|----------------|
| Fraction I | 0.5        | Chloroform | 25 c.c.           | +0.62°       | +15.5°         |
| „ VII      | 0.5        | „          | „                 | 1.52         | 38.0           |
| „ I        | 0.5        | Water      | „                 | 1.84         | 46.0           |
| „ VII      | 0.5        | „          | „                 | 2.10         | 52.5           |

Obviously, in spite of their similarity in appearance and melting point, these two fractions contained salts having very different specific rotations, especially in chloroform solution, and the presence of isomerides was distinctly indicated.

In order to ascertain to what extent the fractional crystallisation had effected a separation of these isomerides, fractions II and VI were also dried at 100° and examined in the polarimeter:

|             | Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|-------------|------------|------------|-------------------|--------------|----------------|
| Fraction II | 0.5        | Chloroform | 25 c.c.           | +0.59°       | +14.7°         |
| „ VI        | 0.5        | „          | „                 | 0.80         | 20.0           |
| „ II        | 0.5        | Water      | „                 | 1.86         | 46.5           |
| „ VI        | 0.5        | „          | „                 | 1.86         | 46.5           |

\* A 200 mm. tube was employed in all these polarimetric determinations.

These results indicated that fractions I to V probably consisted of the *ad*-salt only, whilst fraction VI contained a small amount, and fraction VII a larger proportion of the *βd*-isomeride.

*Regeneration of the ad-Salt.*

The first five fractions, which constituted about 85 per cent. of the whole, were next decomposed with barium hydroxide solution, the base distilled in steam and again neutralised with the chloro-acid, which was recovered from the solution of the barium salt. The solution was then concentrated, and the *regenerated* salt systematically crystallised from water and aqueous alcohol as before; it was thus separated into eight fractions, all of which except the last (VIIIa) had been crystallised about eight times.

Fractions Ia and VIIIa were dried at 100°; they then melted at 207° and 200° respectively, and gave the following values when examined optically:

| Fraction | Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|----------|------------|------------|-------------------|--------------|----------------|
| Ia       | 0.5        | Chloroform | 25 c.c.           | +0.63°       | +15.75°        |
| „        | VIIIa      | „          | „                 | 0.72         | 18.0           |
| „        | Ia         | Water      | „                 | 1.83         | 45.7           |

These results seem to show that the regenerated salt was homogeneous, but as this could hardly be the case, fraction VIIa (the last but one), which differed somewhat from the others in appearance, was also examined, and as the following data show, an impure preparation of the missing *βd*-isomeride was thus discovered.

|               |          |            |         |        |        |
|---------------|----------|------------|---------|--------|--------|
| Fraction VIIa | 0.5 gram | Chloroform | 25 c.c. | +1.39° | +34.8° |
|---------------|----------|------------|---------|--------|--------|

This experiment emphasises the importance of examining such salts for the presence of isomerides, and shows also that even when one of the compounds is produced in relatively very small proportion it does not necessarily pass into the final mother liquors when the crude product is systematically crystallised; similar observations have been made in the case of the other salts examined.

Having proved that the chloro-salt regenerated from the pure *ad*-compound contains an isomeride, attempts were made to isolate the latter.

The two fractions, VII and VIIa, of the crude preparation were therefore mixed together and crystallised two or three times from water at the ordinary temperature; a salt was then deposited in opaque, bulky masses of slender needles, barely distinguishable from the partially racemic  $\alpha$ -salt, and some of the mother liquors gave a similar deposit, containing, however, a few much larger prisms, which were

obviously crystals of the *ad*-isomeride. The latter were separated mechanically, the crystallisation from water being repeated several times (without fractionating) until the deposits seemed to be free from the *ad*-compound; the salt was then crystallised twice from water and once from ethyl acetate containing a small quantity of methyl alcohol, the most sparingly soluble portion being separated each time.

A preparation was thus obtained in small, lustrous, anhydrous prisms; it melted sharply at 195—196°, and appeared to be a pure compound.

An optical examination of this preparation (IX), dried at 100°, gave the following results:

|             | Substance. | Solvent.   | $\alpha_D$ . | $[\alpha]_D$ . |
|-------------|------------|------------|--------------|----------------|
| Fraction IX | 0.5        | Chloroform | +1.39°       | +34.7°         |
| "           | "          | Water      | 2.18         | 54.5           |

From the moderately close agreement between these values and those previously obtained with fraction VII (p. 905), which had not been by any means so exhaustively treated, it seemed that the isolation of the pure  $\beta d$ -isomeride had been accomplished. As a matter of fact, however, in spite of appearances to the contrary, the sample (fraction IX) just examined still contained relatively large quantities of the *ad*-isomeride. As this preparation separated from warm concentrated aqueous solutions as an oil, and its purity on that account seemed doubtful, it was again fractionally crystallised from water and thus resolved into 8 or 10 very small portions, some of which, when repeatedly crystallised at the ordinary temperature, occasionally gave one or two prisms of the *ad*-modification; these crystals were separated mechanically, and the residual salt was then further treated, the most sparingly and the most readily soluble portions being rejected; it was finally precipitated from its concentrated solution in hot methyl alcohol by the addition of ethyl acetate, and separated into two fractions, X and XI; the mother liquors from the last fraction (XI) seemed to be free from *ad*-salt, as when evaporated to dryness and the residue crystallised from water no prisms of this isomeride could be observed in the deposit.

These two fractions were dried at 100° and examined optically:

|            | Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|------------|-------------------|--------------|----------------|
| Fraction X | 0.5        | Water      | 25 c.c.           | +2.21°       | +55.2°         |
| " XI       | "          | "          | "                 | "            | 55.2           |
| „X + XI    | „          | Chloroform | „                 | 1.39         | 34.8           |

These two samples melted sharply and simultaneously at 195—196°, showing no signs of sintering even at 194°; when crystallised slowly from water or aqueous methyl alcohol, they were deposited in long,



concentrically grouped needles of some size, and the deposits seemed to be homogeneous. From hot solutions, however, the salt still separated as an oil, and it was this behaviour alone which led to its further purification.

The fractions X and XI, having been mixed together, were submitted to another long series of crystallisations from water and aqueous methyl alcohol; in these operations, traces of the *ad*-salt were repeatedly met with, especially when a deposit, which had been formed very slowly, was treated with a very slight amount of methyl alcohol, the solution rapidly decanted, and the residue crystallised from water; combining this method with fractional crystallisation, the pure *βd*-isomeride was ultimately obtained in a crystalline form very different from that of the impure salt; its properties are described on p. 909.

It is very difficult to give even an approximate estimate of the relative proportions of the *ad*- and *βd*-isomerides in the original chloro-salt, owing to the large number of crystallisations required to effect their separation and to the fact that a portion of the *βd*-salt cannot be isolated; roughly speaking, the quantity of pure *βd*-isomeride actually obtained amounted only to about 5 per cent.

*ad*-Hydrindamine d-Chlorocamphorsulphonate.

This isomeride, as already indicated, is obtained in a pure condition without any difficulty by repeatedly crystallising the crude salt from hot water.

The crystals thus obtained consist of very large, white, fern-like masses of small, ill-defined, hydrated prisms; from cold solutions in water or aqueous alcohol, the salt is deposited in well-defined, six-sided, transparent crystals, but when they attain a considerable size they often have a rather curious appearance and consist of an opaque, white core surrounded by transparent parts.

Samples of the crystals from aqueous solution, which were dried in the air, and had apparently slightly effloresced, were heated at 100°.

1.139 lost 0.0435 at 100°;  $H_2O = 3.8$  per cent. ( $1H_2O$  requires 4.3 per cent.)

From its solution in methyl alcohol, the salt is precipitated on adding ethyl acetate in the form of slender, well-defined, apparently anhydrous prisms indistinguishable by inspection from the crystals of the *βd*-isomeride obtained in a similar manner.

The *ad*-salt is very readily soluble in boiling water, and does not separate as an oil from hot saturated solutions; it dissolves freely in cold chloroform. Its specific rotation in aqueous solution is  $[\alpha]_D + 46^\circ$ , and in chloroform  $[\alpha]_D + 15.5^\circ$ .

The great difference in appearance between the hydrated crystals

of this *ad*-salt and the anhydrous crystals of the corresponding bromo-salt (p. 878) is very noteworthy; the difference between this salt and its *βd*-isomeride is also remarkable considering the probable similarity between the *ad*- and *βd*-isomerides of the bromo-salt.

*βd-Hydrindamine d-Chlorocamphorsulphonate.*

The pure salt separates from water in long, lustrous needles or prisms, absolutely different in appearance from the bulky, opaque masses which are formed when a small proportion of the *ad*-isomeride is present, and it does not separate as an oil even from hot saturated solutions. The crystals from aqueous solution are hydrated; when rapidly heated, they generally melt at 100° in their water of crystallisation.

0.5014 air-dried salt lost 0.0198 at 100°.  $H_2O = 3.9$ .

$C_{10}H_{14}OCl \cdot SO_3H, C_9H_{11}N, H_2O$  requires  $H_2O = 4.3$  per cent.

From a solution in methyl alcohol, ethyl acetate precipitates the *βd*-salt in small, transparent, apparently anhydrous prisms melting at 202—203°. It is very readily soluble in alcohol and chloroform, but only sparingly so in cold water.

Determinations of the specific rotation were made with a sample of the salt which seemed to be pure, and which was previously dried at 100°:

| Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|--------------|----------------|
| 0.4816     | Chloroform | 25 c.c.           | +1.9°        | +49.3°         |
| "          | Water      | "                 | 2.27         | 58.8           |

The great difference between the value  $[\alpha]_D + 49.3^\circ$  and those (+38°, +34.7°, +34.8°) previously obtained in chloroform solution with samples of the impure salt, show that the latter must have contained a very large proportion of the *ad*-isomeride in spite of its apparent homogeneity. The value in aqueous solution is remarkably high, and corresponds with a molecular rotation  $[M]_D + 235^\circ$ ; since the basic ion has no appreciable optical activity in the *ad*-isomeride, and the molecular rotation of the acid is only  $[M]_D + 188^\circ$  (Trans., 1900, 77, 902), it may be inferred that the salt is only very partially dissociated.

The most striking difference between this *βd*-salt and its *βl*-isomeride is that the crystals of the latter are anhydrous, even when deposited from aqueous solution.

*Formation and Separation of the al- and βl-Isomerides.*

The *l*-base, obtained by decomposing the pure *al*-modification of hydrindamine bromocamphorsulphonate with barium hydroxide solution,

is neutralised with pure chlorocamphorsulphonic acid (prepared from its ammonium salt) and the solution concentrated; on cooling, the product is deposited in long, transparent needles, indistinguishable by inspection from those of the  $\alpha$ *l*-form of hydrindamine bromocamphorsulphonate; the mother liquors are again evaporated, and the first and subsequent deposits systematically crystallised from water in the usual manner.

When the salt is thus separated into seven fractions, each of which except the last (VII), which is obtained from the final mother liquors, has been crystallised six times, there is no appreciable difference in appearance between them, and they all melt at about 117–119°, the last fraction, perhaps, not quite so sharply as the first.

The first fraction was now crystallised three times from water and three times from aqueous methyl alcohol, a considerable proportion being left in solution each time; it was then dried at 100° and examined in the polarimeter, with the following results:

|            | Substance. | Solvent.   | Vol. of solution. | $\alpha_D^{25}$ | $[\alpha]_D^{25}$ |
|------------|------------|------------|-------------------|-----------------|-------------------|
| Fraction I | 0.5        | Water      | 25 c.c.           | +1.77°          | +44.25°           |
| "          | "          | Chloroform | "                 | 1.81            | 45.25             |

Only about 8 per cent. of the original salt remained when this preparation was finally crystallised three times from water, the optical properties of the final fraction being practically identical with those of Fraction I, as shown by the following data:

| Substance. | Solvent.   | Vol. of solution. | $\alpha_D^{25}$ | $[\alpha]_D^{25}$ |
|------------|------------|-------------------|-----------------|-------------------|
| 0.5        | Water      | 25 c.c.           | +1.77°          | +44.25°           |
| "          | Chloroform | "                 | 1.83            | 45.7              |

This preparation consists of the pure  $\alpha$ *l*-isomeride, the properties of which are described later (p. 912).

The further examination of the salt contained in fractions II to VII at first failed to reveal the presence of an isomeride, but on separating the portions IV to VII into about ten fractions by crystallising from water, a slight difference in appearance between some of them might be observed, namely, that certain deposits contained tufts, which were composed of somewhat smaller needles than usual, and which consequently formed translucent, rather than transparent, aggregates. As it was not possible to separate these tufts from the confused crystalline mass by any mechanical process, those deposits which seemed to be similar were added together and this mixture again fractionally crystallised from water; some of the fractions thus obtained seemed to consist of pure  $\alpha$ *l*-salt and were rejected, whilst others were richer in the translucent tufts and were collected separately; there was, however, no apparent connection between the appearance of a fraction



and its solubility, as when systematic crystallisation was again attempted, of six successive deposits, the second and fifth, for example, might give a considerable quantity of the tufts, but all the others yielded very little.

Guided, however, by the almost inappreciable difference in appearance (which is not readily described), samples, consisting largely of tufts, were ultimately obtained, and these, after several further crystallisations from water, gave deposits of small, transparent needles, indistinguishable in appearance from those of the *α*-salt, but which always began to form at the bottom instead of at the surface of the solution; the melting point of these deposits now began to differ from that of the *α*-isomeride, and to range from about 120° to 130°; crystallisation from aqueous alcohol raised the melting point to 135–140°.

A sample of the salt thus obtained in relatively very small quantities and having a melting point of about 136° was dried at 100° and examined in the polarimeter; as there was only 0.6 gram of this preparation, the salt recovered from the chloroform solution was used for the determination in water:

| Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|--------------|----------------|
| 0.5        | Chloroform | 25 c.c.           | +2.34°       | +58.5°         |
| „          | Water      | „                 | 2.25         | 56.5           |

These values differ widely from those obtained with the samples of *α*-salt (m. p. 118–119°), and prove the existence of the *β*-isomeride.

The final purification of this *β*-salt is a simple matter; after several recrystallisations from aqueous methyl alcohol, it is obtained in what is doubtless a state of purity, and its properties are described later (p. 912).

It is rather noteworthy that, although the isomeric *α*- and *β*-chloro-salts differ in melting point by about 20°, their separation from one another is a far more difficult task than that of the corresponding bromo-isomerides, and is only equalled by the difficulty of isolating the *β*-modification of the chloro-salt; even after the experience gained in the cases just mentioned, it was some time before the *β*-salt was successfully isolated.

The quantity of the *β*-isomeride in the original salt probably does not amount to 10 per cent., and of this a considerable proportion cannot be separated from the *α*-modification; the two compounds seem, in fact, to form mixed crystals which break up and become opaque when heated with water; this behaviour serves as a useful indication of the presence of the *β*-salt in the deposits.

*Regeneration of the  $\alpha$ -Salt.*

In order to obtain further quantities of the  $\beta$ *l*-isomeride, and also to make certain that this substance is really composed of *l*-hydrindamine and a pure *d*-chloro-acid identical with that contained in the  $\alpha$ *l*-salt, a considerable quantity of the latter, which had been exhaustively crystallised and which was doubtless free from  $\beta$ *l*-isomeride, was decomposed with barium hydroxide solution; the chloro-salt was then regenerated from the base, which had been distilled in steam, and from the acid recovered from the barium salt.

This preparation, when fractionally crystallised, behaved in all respects like that previously examined, and the optical examination of a dried sample of the *crude*  $\beta$ *l*-isomeride obtained from it gave the following result:

| Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|--------------|----------------|
| 0.5        | Chloroform | 25 c.c.           | + 2.35°      | + 58.7°        |

 *$\alpha$ l-Hydrindamine d-Chlorocamphorsulphonate.*

In appearance and in its behaviour towards solvents, there is a very close resemblance between the  $\alpha$ *l*-salt of the chloro-acid and that of the corresponding derivative of the bromo-acid.

The  $\alpha$ *l*-chloro-salt crystallises from water in long, slender, anhydrous needles, and from cold aqueous methyl alcohol in well-defined, compact prisms. It melts at 118—120° when in the form of moderately large crystals, but if these be crushed to a fine powder, the latter sinters distinctly at about 115°; as a rule, the large crystals melt completely below 121°, but the powder, after sintering, solidifies again, and then melts fairly sharply at 195—196° when heated quickly, without any appreciable charring. These observations seem to show that the salt is dimorphous, and that the ordinary form obtained from solutions is unstable at temperatures above about 115°; as in the case of the corresponding  $\alpha$ *l*-bromo-salt, however, it is difficult to say whether or not this behaviour is due to partial loss of base.

The salt is very readily soluble in cold chloroform and dissolves freely in cold alcohol, but is only sparingly soluble in cold water.

Its specific rotation in a 2 per cent. aqueous solution is  $[\alpha]_D + 44.0^\circ$ , and in chloroform  $[\alpha]_D + 45.5^\circ$ .

 *$\beta$ l-Hydrindamine d-Chlorocamphorsulphonate.*

The two preparations of *crude*  $\beta$ *l*-salt, obtained as already described (p. 911 and above), were mixed and repeatedly crystallised from water

and aqueous methyl alcohol until their mother liquors gave homogeneous deposits; the pure compound was thus obtained in long needles.

A sample, dried at  $100^{\circ}$ , gave the following optical values:

| Substance. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|------------|-------------------|--------------|----------------|
| 0.5        | Chloroform | 25 c.c.           | +2.42°       | +60.5°         |
| „          | Water      | „                 | 2.30         | 57.5           |

Further crystallisation was not considered necessary, as the salt resembles the corresponding  $\beta$ l-bromo-compound so closely that its appearance was deemed to be sufficient evidence of its purity.

The  $\beta$ l-chloro-salt is readily soluble in methyl alcohol, from which it is deposited in coarse, ill-defined prisms; it seems to be less soluble in hot water than any of its isomerides, and from very concentrated hot solutions it crystallises in felted masses of very slender needles; it dissolves freely in cold chloroform.

Its melting point, like that of the  $\beta$ l-bromo-salt, is very indefinite and varies greatly with the size of the crystals; the coarse prisms obtained from cold solutions in methyl alcohol generally melt fairly sharply and completely at  $145$ — $146^{\circ}$ , but when crushed to a fine powder the same preparation melts at  $130$ — $133^{\circ}$ ; occasionally the fused mass solidifies again when left in the hot bath and melts for a second time at about  $232^{\circ}$ , but these indications of dimorphism have not been very closely studied.

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## LXXXIX.— $\alpha$ -Amino- $\beta$ -methylhydrindene.

By FREDERIC STANLEY KIPPING and GEORGE CLARKE, A.I.C.

THE method already employed with such success for the synthesis of the cyclic ketones,  $\alpha$ -hydrindone (Kipping, Trans., 1894, 65, 680),  $\alpha$ -ketotetrahydronaphthalene (Kipping and Hill, Trans., 1899, 75, 144), and pheno- $\alpha$ -ketoheptamethylene (Kipping and Hunter, Trans., 1901, 79, 602), from the chlorides of aliphatic acids containing aromatic substituents has now been extended to the preparation of substituted ketones, and in the present paper the authors describe the results of experiments on the intramolecular condensation of benzylmethylacetic chloride under the influence of aluminium chloride.



The  $\beta$ -methyl- $\alpha$ -hydrindone, which is thus produced,



contains an asymmetric carbon group, and consequently the synthetical compound is composed of equal quantities of enantiomorphously related components. When, therefore, it is combined with hydroxylamine and the resulting oxime reduced to the base  $\beta$ -methyl- $\alpha$ -hydrindamine ( $\alpha$ -amino- $\beta$ -methylhydrindene), a homologue of hydrindamine, the product will contain two asymmetric carbon groups, a new one having been formed during the reduction of the oximino- to the amino-group,



From theoretical considerations, then, the base should exist in four optically active modifications, namely :

| I. | II. | III. | IV. |
|----|-----|------|-----|
| +  | -   | +    | -   |
| +  | -   | -    | +   |

and these should give rise to two different externally compensated compounds formed by the admixture of I and II, and of III and IV respectively.

When combined with optically inactive acids, the synthetical base should therefore give two series of salts, and, as will be shown later, two hydrochlorides are in fact produced, but in very unequal quantities; this formation of unequal quantities of the two *dl*-bases is, of course, what might have been expected, inasmuch as the synthesis of the second asymmetric carbon group occurs in a compound which is already enantiomorphous.

The principal object in preparing these bases was to study their behaviour with optically active acids, and to obtain, if possible, isomeric partially racemic salts corresponding with the hydrindamine compounds (Kipping, *Trans.*, 1900, 77, 861); as one of the authors was unfortunately unable to continue the work, the thorough investigation of some salts of the two bases is described in the following paper.

$\beta$ -Methyl- $\alpha$ -hydrindone has been previously prepared by von Miller and Rhode (*Ber.*, 1890, 23, 1888) by heating benzylmethylacetic acid with concentrated sulphuric acid at  $150^\circ$ ; this method, however, was found to be unsatisfactory, as the yield was very poor compared with that obtained with the aid of aluminium chloride.

## EXPERIMENTAL

Benzylmethylacetic acid is conveniently obtained from benzylmethylmalonic acid by eliminating carbon dioxide, or by the acid hydrolysis of ethyl benzylmethylacetoacetate; the acid boils at  $160-161^{\circ}$  under a pressure of 17 mm., and solidifies when cooled to a mass of colourless crystals melting at  $37^{\circ}$ , as stated by Conrad and Hodgkinson (*Annalen*, 1878, 193, 312).

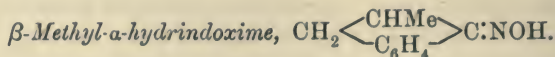
*Benzylmethylacetic chloride* is prepared with the aid of phosphorus pentachloride in the usual manner, a vigorous action taking place; it is a moderately mobile liquid, fumes slightly on exposure to the air, and has a particularly disagreeable and penetrating odour.

*Preparation of  $\beta$ -Methyl- $\alpha$ -hydrindone.*

The action of aluminium chloride on benzylmethylacetic chloride and the amount of methylhydrindone produced depend entirely on the conditions of the experiment. The action is not so vigorous as that which occurs in the preparation of hydrindone, and, probably in consequence of this, the formation of tarry matter is not nearly so great.

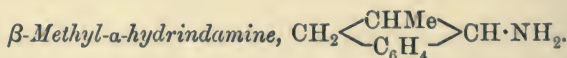
In the first experiments, the acid chloride was dissolved in five times its volume of light petroleum (b. p.  $60-80^{\circ}$ ), and three parts of aluminium chloride employed to five of the acid chloride; no evolution of hydrogen chloride occurred, however, and not until the mixture had been heated for some time did any action begin. A colourless, crystalline compound, non-volatile in steam, was then formed, but as this substance, doubtless an aluminium compound, was not decomposed, giving the ketone, when boiled with weak alkalis, it was not further investigated. After further experiments, the following were found to be the best conditions for the production of the desired ketone. The acid chloride (10 grams), dissolved in from 6—7 times its volume of light petroleum (b. p.  $90-100^{\circ}$ ), is treated with finely powdered aluminium chloride (10 grams), and the mixture gradually heated on the water-bath until the petroleum begins to boil, the flask being vigorously shaken in the meanwhile. At the end of fifteen minutes, the evolution of hydrogen chloride, which has previously been very vigorous, begins to slacken, and in about twenty minutes the reaction may be considered to be complete. After cooling, water is cautiously added, and the light petroleum distilled off in a slow current of steam; the ketone is then distilled in steam, the distillate rendered alkaline with sodium carbonate, and the ketone extracted with ether. The product remaining after evaporating the ether is a colourless oil,

having the strong odour of peppermint mentioned by von Miller and Rhode; the yield is 70—80 per cent. of the theoretical.



This oxime is prepared in the usual manner, the ketone being treated with hydroxylamine hydrochloride and excess of caustic potash in aqueous methyl-alcoholic solution; after 24 hours at the ordinary temperature, most of the alcohol is evaporated off on the water-bath, and the mixture is poured into water, when the oxime separates as a red, viscid oil, which very slowly solidifies to a hard cake.

The crude product, crystallised either from aqueous methyl alcohol or light petroleum, is thus obtained in well-defined, apparently octahedral crystals melting at about 104°; it is readily soluble in alcohol, ether, and chloroform, but only sparingly so in cold light petroleum, being almost insoluble in water and alkalis. The further investigation of this compound showed that it consisted of a mixture of isomerides which, however, were not isolated; samples of the material, roughly purified by one crystallisation, were employed for the preparation of the base.



*β*-Methylhydrindoxime is readily reduced with the aid of sodium amalgam and aqueous acetic acid; in order to avoid waste of amalgam, the solution should be kept cool and stirred continuously, the amalgam being added in small quantities at a time. When only a slight turbidity is formed on the addition of water, the solution is decanted, and any unchanged oxime distilled off in a current of steam; the base is then liberated by adding excess of caustic potash and the steam distillation continued.

The *β*-methyl-*α*-hydrindamine then passes over as a colourless oil, which has a strong odour not unlike that of aniline and is only sparingly soluble in water; it is a strong base, and on exposure to the air it is converted into a crystalline substance owing to absorption of carbon dioxide.

#### *The Two dl-β-Methyl-α-hydrindamines.*

As pointed out above, two bases should be formed by the reduction of the oxime, but not necessarily in equal quantities. It was, however, a matter of some doubt whether the difference in solubilities of their salts with optically inactive acids would be such as to render possible a separation of these salts by fractional crystallisation.



With the view of ascertaining whether or not this was the case, the mixture of bases and water obtained by distillation in steam was treated with hydrochloric acid and the resulting product systematically crystallised from water. The first and several successive deposits consisted of long, silky needles, which were apparently homogeneous, but subsequent fractions were obviously mixtures and contained, in addition to the long needles, small, nodular masses of smaller and ill-defined crystals. After further recrystallisation, the hydrochloride separating in long needles was obtained in an apparently pure condition; it had not a definite melting point, but decomposed at about  $250^{\circ}$ . This compound is referred to as the hydrochloride of the *A*-base. The hydrochloride crystallising in nodular masses, which is referred to as the salt of the *B*-base, was probably only obtained in an impure condition; it decomposed at about  $225^{\circ}$ .

#### *The Platinichlorides of the Two dl-Bases.*

In order to prove that the hydrochlorides just described are derived from isomeric bases, analyses of the platinichlorides were made. The *platinichloride* prepared from the hydrochloride of the *A*-base crystallised from water in lustrous, yellow plates decomposing at about  $192^{\circ}$ ; a sample which had been crystallised twice from water and air-dried until constant in weight was analysed, with the following results:

0.3457 lost 0.0157 at  $100^{\circ}$ .  $H_2O = 4.54$ .

0.2461 „ 0.0121 at  $100^{\circ}$ .  $H_2O = 4.91$ .

0.3284 anhydrous salt gave 0.0905 Pt. Pt = 27.55.

$(C_{10}H_{13}N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$  requires  $H_2O = 4.81$ ; Pt = 27.68 per cent.

The *platinichloride* prepared from the hydrochloride of the *B*-base was rather more soluble in water than the derivative of the *A*-base, and separated in lustrous, yellow plates decomposing at about  $202^{\circ}$ ; the air-dried salt did not lose in weight when heated at  $100^{\circ}$ .

0.4304 gave 0.1190 Pt. Pt = 27.64.

$(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$  requires Pt = 27.68 per cent.

#### *The Benzoyl Derivatives of the Two dl-Bases.*

As it was difficult to tell whether the hydrochlorides were pure or not, that is to say, whether the two *dl*-bases had been completely or only partially separated, the benzoyl derivatives were prepared from samples of the two hydrochlorides by the Schotten-Baumann method. The crude products, which were precipitated in the form of colourless powders, were purified by crystallisation from alcohol.

The *benzoyl* derivative of the *A*-base was thus obtained in long, silky needles melting sharply at  $169^{\circ}$ , and its melting point was not changed on repeated crystallisation; it was only sparingly soluble in cold alcohol, but dissolved freely on warming.

The *benzoyl* derivative of the *B*-base crystallised in short needles, and was apparently much more readily soluble in alcohol than the derivative of the *A*-base; it began to melt at about  $135^{\circ}$  and liquefied completely at about  $138^{\circ}$ , but when fractionally crystallised its melting point did not remain constant and it was doubtless a mixture of the two isomerides. Attempts to isolate a pure compound from this mixture were not successful, but the above experiments seemed to establish the existence of two externally compensated methylhydrindamines.

The cost of part of the materials used in this work was covered by a Government Grant from the Royal Society, for which the authors desire to record their thanks.

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*XC.—Isomeric Partially Racemic Salts Containing Quinquevalent Nitrogen. Part XI. Derivatives of dl-Methylhydrindamine and dl-neo-Methylhydrindamine. Isomeric Salts of the Type  $NR_1R_2H_3$ .*

By GEORGE TATTERSALL, B.Sc., and FREDERIC STANLEY KIPPING.

THE preliminary examination of the methylhydrindamine which is produced by the reduction of methylhydrindoxime having shown that this base is a mixture of isomerides (Kipping and Clarke, this vol., p. 917), the next step was to separate and obtain in a pure condition the two structurally identical, externally compensated compounds of which, according to theory, the mixture is composed; it would then be possible to proceed further and to study the partially racemic salts which, it was hoped, would be obtained either from one or both of the bases, and which would probably be of the same interesting character as those formed from *dl*-hydrindamine (Kipping, *Trans.*, 1900, 77, 861; 1901, 79, 430). The first attempts to separate the two *dl*-bases from one another were only partially successful. In the first instance, wishing to avoid the use of an optically active acid, because this might have given rise to a mixture of many different salts, the separation of which would probably be a matter of some difficulty, we first tried fractional

crystallisation of the sulphate, benzoate, cinnamate, picrate, and other salts prepared from the crude basic mixture; it was found, however, that none of these salts gave a more satisfactory result than that obtained with the hydrochloride (Kipping and Clarke, *loc. cit.*) and the experiments were therefore abandoned.

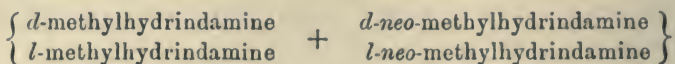
We next examined the salts obtained by combining the base with various, optically active acids and in the end succeeded in effecting a complete separation of the two *dl*-bases with the aid of *d*-bromocamphorsulphonic acid. Although, as will be shown later, this acid gives rise to at least six, and probably eight methylhydrindamine bromocamphorsulphonates, yet systematic fractional crystallisation, combined with mechanical sorting, results in the isolation of two salts, each of which has the outward properties of a distinct and single substance. One of these methylhydrindamine bromocamphorsulphonates, namely, that which is present in the much larger quantity, crystallises from water in hydrated, somewhat ill-defined, prismatic crystals, but is deposited from some solvents in long, well-formed, transparent prisms; the other bromocamphorsulphonate separates from water and dilute alcohol in magnificent, broad, transparent, well-defined, anhydrous masses, totally different from the crystals of the first in outward characteristics. Each of these salts is a *partially racemic* compound; the fractional crystallisation of the original mixture does not result in a resolution of either of the *dl*-bases, but merely gives a separation of the two externally compensated compounds; the optically active acid, therefore, plays the part of an optically inactive acid, but is more effective since with its aid each of the *dl*-bases is freed from its isomeride.

The fact that each of the two bromocamphorsulphonates is partially racemic is established in various ways; when decomposed, they both give bases which are optically inactive; the base from the one gives with optically inactive compounds derivatives which are different from those of the base from the other bromocamphorsulphonate, showing that the two bases are not enantiomorphously related.

Before proceeding further, it will be advisable to distinguish between these two externally compensated bases, and we propose to do so by naming one  $\beta$ -methyl- $\alpha$ -hydrindamine, the other *neo*- $\beta$ -methyl- $\alpha$ -hydrindamine; the letters  $\alpha$  and  $\beta$  have, of course, a structural significance and refer to the positions of the amino- and methyl-groups respectively in the hydrindamine ring; they will not be used again, except when necessary in order to avoid confusion. The term *neo*- is employed in default of a better one, because it has already been used by Forster in the case of the two bornylamines (Trans., 1898, 63, 391), the relationship between which is exactly comparable with that between the two methylhydrindamines; as there is no available means of deciding which of the methylhydrindamines corre-



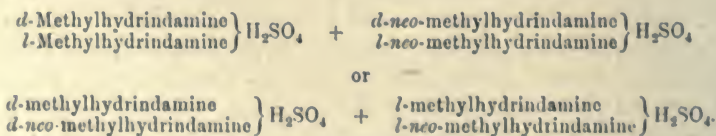
sponds with bornylamine and which with *neo*-bornylamine, we apply this prefix to that *dl*-base which is produced in the smaller proportion. The original mixture consists, therefore, of



The two bases, *dl*-methylhydrindamine and *neo-dl*-methylhydrindamine show, as was only to be expected, a great similarity in ordinary chemical behaviour and also resemble *dl*-hydrindamine very closely; they have been sufficiently characterised by an examination of their hydrochlorides, sulphates, picrates, and benzoyl derivatives, the properties of which are summarised in the following table.

|                          | <i>dl</i> -Methylhydrindamine.                          | <i>dl-neo</i> -Methylhydrindamine.                    |
|--------------------------|---|---|
| Hydrochloride .....      | { Needles; beginning to char<br>about 230°.             | { Needles; beginning to<br>char about 235°.           |
| Sulphate .....           | { Long needles; melting and<br>decomposing at 233—235°. | { Plates; melting and de-<br>composing at about 220°. |
| Picrate .....            | { Yellow prisms; decomposing<br>at about 230°.          | { Yellow prisms; decom-<br>posing at 195—196°.        |
| Benzoyl derivative ..... | Needles; m. p. 151°.                                    | Needles; m. p. 169°.                                  |
| Bromocamphorsulphonate   | { Rhomboidal prisms; m. p.<br>170°.                     | { Large, broad prisms; m. p.<br>194°.                 |

It may perhaps be mentioned that in attempting the separation of the two *dl*-bases by the fractional crystallisation of their sulphates a normal salt was obtained in large, well-defined, tabular crystals of considerable size. It was thought at first that this salt was a pure derivative of one of the *dl*-bases only, as it did not change its characteristic appearance when fractionally crystallised from water. It was nevertheless a mixture of the sulphates of *dl*-methylhydrindamine and of *dl-neo*-methylhydrindamine, and therefore possibly consisted of four components, in spite of its apparent homogeneity; this fact is noteworthy, and indicates the existence of a type of compound which may be classed as *doubly racemic*, since it may be regarded as composed of two pairs of enantiomorphously related substances; in some respects, this complex sulphate may be regarded as analogous to the  $\beta$ -modification of hydrindamine bromocamphorsulphonate, but in the case of the latter, no two of the components are enantiomorphously related. The composition of the sulphate may be represented thus:



Having prepared considerable quantities of the bromocamphor-

sulphonate of methylhydrindamine and of *neo*-methylhydrindamine in a pure condition, we entered on the most important stage of this investigation, namely, the examination of these and other salts of the bases, in order to ascertain whether they existed in isomeric forms. The first question to settle was whether either of the bases gave rise to isomeric partially racemic salts analogous to those obtained from hydrindamine. This question could hardly be answered with certainty by examining the mixture of salts left in the mother liquors after separating the two bromocamphorsulphonates, but was easily settled in the following manner. Pure methylhydrindamine bromocamphorsulphonate was decomposed with barium hydroxide and the liberated base neutralised with bromocamphorsulphonic acid; the product was identical with the original salt in all ordinary properties, and could not be resolved into appreciably different fractions by crystallisation. A similar experiment, made with pure *neo*-methylhydrindamine bromocamphorsulphonate, gave similar results; the regenerated salt was apparently identical with the original one, and owing to the well-defined character of this compound the presence of isomerides could not be easily overlooked.

Now, since the regeneration of either of the partially racemic hydrindamine bromocamphorsulphonates or chlorocamphorsulphonates invariably results in the formation of two salts ( $\alpha$  and  $\beta$ ), we conclude that methylhydrindamine and *neo*-methylhydrindamine do not give isomeric partially racemic compounds with the bromocamphorsulphonic acid.

The resolution of the partially racemic salts was then attempted; crystallisation from water, dilute alcohol, &c., having been found to be useless, the salts were treated with boiling ethyl acetate under conditions similar to those employed in the case of the hydrindamine compounds. The *neo*-methylhydrindamine salt was very refractory, and up to the present we have failed to resolve it; the methylhydrindamine salt, however, afforded two components, the one separating from the hot solution, the other remaining in the mother liquors; as in the case of the hydrindamine salts, the resolution is very incomplete, and the isolation of that component which remains in the solution is a somewhat troublesome process. These two components of the partially racemic methylhydrindamine bromocamphorsulphonate are remarkably similar in ordinary properties; they separate from water in slender prisms, are indistinguishable by inspection, and have only slightly different melting points, the one liquefying at about  $230^{\circ}$ , the other at about  $249^{\circ}$ .

The former is the one which separates from the hot ethyl acetate solution; it is a salt of the *l*-base, and is therefore termed the *l*-component. Its molecular rotation is about  $[M]_D + 209^{\circ}$  in dilute



aqueous solution, so that the molecular rotation of the basic ion should be about  $[M]_D - 61^\circ$ ; a solution of the free base in aqueous alcohol shows a laevorotation.

The latter (m. p.  $249^\circ$ ) is a salt of the enantiomorphously related *d*-methylhydrindamine, and is referred to as the *d*-component; its molecular rotation in dilute aqueous solution is  $[M]_D + 326^\circ$ , that of the basic ion, therefore, should be  $[M]_D + 56^\circ$ ; the free base is dextro-rotatory in aqueous alcoholic solution.

So far, the examination of the partially racemic methylhydrindamine bromocamphorsulphonate failed to show any analogy with the hydrindamine salts; the *dl*-base formed but one partially racemic salt, and this appeared to consist of two components only; in fact, the base apparently behaved in a perfectly normal manner.

Further investigation showed, however, that each of the components (m. p.  $230^\circ$  and  $249^\circ$  respectively) of the partially racemic salt is itself a mixture of two isomerides; consequently, the partially racemic methylhydrindamine bromocamphorsulphonate, although an apparently homogeneous substance, is, in reality, a mixture of *four* different substances, just as is the partially racemic  $\beta$ -salt of hydrindamine and *d*-bromocamphorsulphonic acid. It belongs, therefore, to the class of *partially di-racemic* salts. Unfortunately, we have not been able to obtain all these isomerides in a state of purity, but we believe we have isolated two of them, *ad* and *al*, and have conclusively established the existence of two others,  $\beta d$  and  $\beta l$ , in the following manner. The *l*-component (m. p.  $230^\circ$ ), when systematically crystallised from water, is very slowly separated into fractions differing slightly in melting point and in specific rotation. After some thirty or forty crystallisations, the first or most sparingly soluble fraction melts at  $236^\circ$  and gives  $[\alpha]_D + 47^\circ$  in water or  $[M]_D 216-217^\circ$ . The original *l*-component (m. p.  $230^\circ$ ), therefore, is not homogeneous. This fact cannot be explained by assuming the presence of *neo*-methylhydrindamine bromocamphorsulphonate or that of the partially racemic methylhydrindamine bromocamphorsulphonate, firstly, because these two salts differ widely from the *l*-component in crystalline form and solubility, and secondly, because they have both a higher specific rotatory power than the *l*-component, and their removal would therefore *lower* and not raise the specific rotation of the latter. The presence of any ordinary impurity in the original *l*-component melting at  $230^\circ$  is absolutely out of the question, considering the manner in which this salt is prepared. All doubt, however, as to the real nature of this *l*-component is easily removed by a crucial experiment; if the *l*-component of methylhydrindamine bromocamphorsulphonate consists of isomeric *al*- and  $\beta l$ -salts corresponding with those of hydrindamine, then either of these salts when decomposed and regenerated should



give rise to a mixture of the two isomerides. This was proved to be the case.

A large quantity of the *l*-component, obtained by resolving the partially racemic salt, was repeatedly crystallised from water, and thus resolved into a large number of fractions, the melting points of which fell gradually from  $236^{\circ}$  to about  $230^{\circ}$ . The lower fractions, in which careful examination failed to detect any impurity, were placed aside, and crystallisation continued until the melting point of the salt did not change. The sample of *l*-component thus obtained, which had probably been crystallised some twenty times and which melted at  $236^{\circ}$ , was then decomposed and regenerated from the *same* acid and the *same* base; the product melted indefinitely at  $230$ – $234^{\circ}$ , and proved to be a mixture like the original *l*-component obtained by the resolution of the partially racemic salt; when systematically crystallised from water and separated into about eight fractions, the first (sparingly soluble) and the last (readily soluble) were different in melting point and specific rotation, as shown by the following data:

|       | M. p.               |                           |
|-------|---------------------|---------------------------|
| First | $236^{\circ}$       | $[\alpha]_D + 47^{\circ}$ |
| Last  | about $230^{\circ}$ | $[\alpha]_D + 44^{\circ}$ |

These results prove conclusively that the *l*-methylhydrindamine gives rise to isomeric  $\alpha$ - and  $\beta$ -salts when it is combined with bromocamphorsulphonic acid, just as does *l*-hydrindamine.

The examination of the *d*-component of the partially racemic methylhydrindamine bromocamphorsulphonate was carried out in an exactly similar manner, and the results were in full accordance with those just described; the original *d*-component is a mixture, and is resolved into different fractions by repeated crystallisation from water; when, moreover, a given sample of this salt which has been repeatedly crystallised is decomposed and regenerated, it is no longer a homogeneous substance, but a mixture of the  $\alpha$ - and  $\beta$ -isomerides.

If any further evidence of the existence of these four isomerides is required, it is afforded by the following fact: when a sample of the most sparingly soluble fraction of the regenerated *l*-component is mixed with an equal quantity of the most sparingly soluble fraction of the *d*-component, and the mixture crystallised from water, the partially racemic salt which is obtained differs in a marked manner from that which affords the original *d*- and *l*-components, as shown below:

|  | Crystalline form.        | M. p.                 | $[\alpha]_D$ in water. |
|--|--------------------------|-----------------------|------------------------|
| Original partially racemic salt.....     | Rhomboidal prisms        | $160$ – $165^{\circ}$ | $+51^{\circ}$          |
| Synthetical partially racemic salt ..... | Long, rectangular prisms | $206^{\circ}$         | $+60^{\circ}$          |

This, of course, must be the case; the original salt is composed of four, the synthetical salt of only two isomerides. The partially racemic methylhydrindamine bromocamphorsulphonate, therefore, corresponds very closely with the partially racemic  $\beta$ -modification of hydrindamine bromocamphorsulphonate and, like the latter, contains four isomerides, which may be distinguished as the *ad*-, *al*-,  $\beta$ *l*-, and  $\beta$ *d*-salts respectively; of these, we have obtained two, namely, the *ad*- and *al*-forms, in a pure condition, but have been unable to isolate the two  $\beta$ -modifications, because they form mixed crystals with the corresponding  $\alpha$ -forms. The behaviour of the mixture of the *al*- and  $\beta$ *l*-salts, as well as that of the *ad*- and  $\beta$ *d*-isomerides, is, in fact, exactly analogous to that of the mixture of the *ad*- and  $\beta$ *d*-hydrindamine bromocaraphorsulphonates. That the  $\beta$ -forms exist in the regenerated salts we are quite convinced, and we believe the experimental evidence on this point to be conclusive; it is extremely probable, nevertheless, that the occurrence of such isomerides would have passed undetected had it not been for the knowledge gained in the examination of the hydrindamine salts.

The analogy between the partially racemic  $\beta$ -salts of methylhydrindamine and of hydrindamine is further shown by an examination of their optical properties. The salt of methylhydrindamine has a molecular rotation  $[M]_D + 236^\circ$ , that of hydrindamine a molecular rotation  $[M]_D + 220^\circ$ , whereas the theoretical molecular rotation is  $[M]_D + 270^\circ$  in both cases. These values for the salt, however, are the mean proportional values of four components, and as shown already the  $\beta$ *d*- and  $\beta$ *l*-forms of hydrindamine bromocamphorsulphonate have abnormally low molecular rotations, namely, less than  $[\alpha]_D + 50^\circ$  and  $+39^\circ$  respectively, whilst the *ad*- and *al*-forms both give  $[M]_D + 270^\circ$  approximately. Now in the case of the methylhydrindamine salts, the *ad*- and *al*-modifications give  $[M]_D + 216^\circ$  and  $+336^\circ$  respectively, so that as the basic ion has a molecular rotation of  $[M]_D + 56^\circ$ , the values may be regarded as normal; the crude samples of  $\beta$ *d*- and  $\beta$ *l*-, however, give  $[M]_D + 203^\circ$ , and  $[M]_D + 314^\circ$  respectively, and as these samples probably contain relatively small quantities of the  $\beta$  components, it may be inferred that the latter have much lower molecular rotations than the calculated values.

#### EXPERIMENTAL.

Previous experiments (Kipping and Clarke, this vol., p. 917) having shown that only one of the *dl*-methylhydrindamines in the basic mixture (resulting from the reduction of methylhydrindoxime) could be isolated in a pure state even by a long continued fractional crystallisation of the hydrochlorides, we prepared the benzoates,



cinnamates, and picrates in order to try and obtain a better method of separating the two bases. All these salts, however, proved to be unsuitable; the two benzoates crystallised together, as did also the picrates, whilst the cinnamates underwent hydrolytic dissociation.

The *normal sulphate* prepared from the basic mixture was fractionally crystallised from water, but all the deposits had the same form consisting of large, tabular crystals and were transparent. The temperature of fusion and decomposition of all the fractions were also identical and had the value 198—205°. It seems, therefore, that the sulphate contains both racemic bases, and is a doubly racemic salt of the nature already indicated (p. 920). That separation of the racemic bases is not effected by this means is further shown by comparing the decomposing point and crystalline form of this salt with those of the sulphates of the separate bases. The latter decompose at 233—235° and 220°, and crystallise in needles and hexagonal plates respectively.

*Bromocamphorsulphonates of the dl-Methylhyndramines.*

After failing to find a suitable optically inactive acid for our purpose, we prepared the *d*-bromocamphorsulphonates by adding the acid to the base suspended in water until the solution was just acid. On evaporating and cooling, the solution became milky and an oil separated which, after vigorous stirring, slowly crystallised. The mother liquors were then concentrated and the whole salt obtained in successive fractions. Careful crystallisation of each of these fractions, using water, dilute alcohol, and almost pure alcohol, revealed the presence of two salts, one of which was easily isolated, whilst the other was only separated with some difficulty. Systematic fractional crystallisation having been found to give unsatisfactory results, the mixed salts which remain after separating the principal component were dissolved in alcohol and a little water added (about 2—3 per cent.), the amount of solvent being sufficient to prevent separation of the salt on cooling. On allowing the solution to evaporate spontaneously, the two salts are obtained in different forms, and can be separated mechanically, one being deposited in opaque or translucent needles (generally in clusters) and the other in transparent prisms. It was also found that a preliminary separation of the bases, with the aid of their hydrochlorides, is advisable, and that the hydrochloride which is obtained in the least soluble portions (which should be about one-third or one-fourth of the whole) gives almost entirely the bromocamphorsulphonate which is found in the mother liquors and which crystallises from strong alcohol in transparent prisms.



*dl-Methylhydrindamine Bromocamphorsulphonate,*  
 $C_{10}H_{13}N, C_{10}H_{14}OBr \cdot SO_3H, H_2O.$

This salt, which separates first from a solution of the mixture of bromocamphorsulphonates, and which is present in by far the larger proportion, we have called the salt of methylhydrindamine. It separates from an aqueous solution, if the latter is more than slightly supersaturated in an oily condition, but from aqueous alcohol it is obtained in hydrated rhomboidal prisms, which are often transparent. When crystallised from strong ethyl alcohol, in which the salt is readily soluble, it is obtained in opaque tufts of needles. It is moderately soluble in hot ethyl acetate and also in acetone, from which it separates in transparent, rectangular prisms. The melting point of this salt is very indefinite, and varies with the solvent from which it is crystallised. The hydrated crystals obtained from water melt at  $97^\circ$ , but, if dried previously, at  $160$ — $165^\circ$ . A sample, crystallised from alcohol and ethyl acetate, melted from  $165$ — $170^\circ$ . The highest melting point ever obtained was with the crystals from acetone, which melted at  $171$ — $173^\circ$ . From ethyl acetate, a value as low as  $155$ — $160^\circ$  was obtained. In spite of these variations in melting point, which are possibly due to decomposition, the salt has the appearance of a homogeneous substance.

A sample of the salt crystallised from dilute alcohol and dried in the air until constant in weight was dehydrated at  $100^\circ$ :

1.1724 lost 0.0427;  $H_2O = 3.64$ : 1.5190 lost 0.0560;  $H_2O = 3.68$ .

$C_{10}H_{13}N, C_{10}H_{14}OBr \cdot SO_3H, H_2O$  requires  $H_2O = 3.7$  per cent.

*Specific and Molecular Rotations of dl-Methylhydrindamine Bromocamphorsulphonate.*

The specific rotation of this salt was determined with different samples dried at  $100^\circ$ .\*

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| 0.4274       | Water      | 25 c.c.           | +1.76°       | +51.5°         | +235.3°   |
| 0.3856       | "          | 25 "              | 1.60         | 51.8           | 236.7     |
| 0.4143       | "          | 25 "              | 1.72         | 51.9           | 237.1     |
| 0.5555       | Chloroform | 20 "              | 2.45         | 44.1           | 201.9     |
| 0.5466       | "          | 20 "              | 2.41         | 44.1           | 201.9     |

The values obtained in aqueous solution seem to show that the salt contains an optically active base having a molecular rotation of

\* A 200 mm. tube was used in all the polarimetric determinations indicated in this communication.

about  $[M]_D - 35^\circ$ , because the molecular rotation of the acid is  $[M]_D + 270^\circ$ .

A portion of the salt was therefore decomposed with barium hydroxide and distilled in steam, the first portions of the distillate collected, a little alcohol added to dissolve the base, and the solution examined in the polarimeter. No appreciable rotation could be detected. Further, a solution of the hydrochloride of this base was also optically inactive. These results seem to be in direct conflict with those obtained in the examination of the bromocamphorsulphonate, but as we shall show later there really is no doubt that the salt is a partially racemic compound and contains equal or approximately equal quantities of the salts of the *d*- and *l*-bases. The homogeneous nature of the base contained in this partially racemic salt, or rather its freedom from *neo*-methylhydrindamine, is proved by the following experiment.

The pure salt was shaken up with benzoyl chloride and caustic potash, and the resulting benzoyl derivative separated and washed. The crude product, when dried, melted at  $150-151^\circ$ , and after several recrystallisations from alcohol, its melting point was still  $151^\circ$ . The substance had further all the characteristics of a pure compound and crystallised in well-defined needles. It was practically insoluble in water, ether, and light petroleum, but moderately soluble in warm alcohol and benzene; it readily dissolved in acetone, chloroform, and hot ethyl acetate.

#### *Salts of dl-Methylhydrindamine.*

Having obtained the *dl*-methylhydrindamine quite free from the isomeric *dl-neo*-base, the following salts were prepared:

The *hydrochloride* which crystallises in long, opaque, shining, needles and decomposes from  $230^\circ$  onwards.

The *normal sulphate* crystallises from water in long needles; it is sparingly soluble in aqueous alcohol and crystallises from this solvent in rhomboidal plates, decomposing at  $233-235^\circ$ .

The *picrate*, prepared by adding a solution of potassium picrate to a solution of either the sulphate or hydrochloride, is sparingly soluble in water and crystallises from alcohol in yellow, almost rectangular plates. It chars from  $220^\circ$  onwards and melts at  $230^\circ$ .

#### *dl-neo-Methylhydrindamine Bromocamphorsulphonate.*

The separation of this salt in a pure condition has been described above. From strong alcohol, it is obtained in transparent prisms, one base of which is at right angles to the edges of the prism, whilst the other is oblique. From water, crystals of the same shape are ob-

tained, but being in masses of small crystals are not generally transparent. The crystals are anhydrous and melt at  $194^{\circ}$ . The salt is readily soluble in hot water, alcohol, chloroform, and acetone, but practically insoluble in ether, light petroleum, and benzene.

*Specific and Molecular Rotations of dl-neo-Methylhydrindamine Bromocamphorsulphonate.*

The following determinations were made with different samples dried at  $100^{\circ}$ :

| Wt. of salt. | Solvent.       | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|----------------|-------------------|--------------|----------------|-----------|
| 0.4763       | Water          | 25 c.c.           | + 2.24°      | + 58.8°        | + 269.3°  |
| 0.4890       | "              | 25 "              | 2.30         | 58.8           | 269.3     |
| 0.4936       | "              | 25 "              | 2.34         | 59.3           | 271.1     |
| 0.6219       | Chloroform     | 20 "              | 3.10         | 49.8           | 228.0     |
| 0.6562       | "              | 20 "              | 3.30         | 50.3           | 230.3     |
| 1.1836       | Methyl alcohol | 25 "              | 6.83         | 72.3           | 331.1     |

The values of the molecular rotation of the salt in dilute aqueous solution seem to show that it is a partially racemic compound. To verify this, a portion of the salt was decomposed with barium hydroxide, and distilled in steam; the base which distilled over was dissolved by adding alcohol, and examined in the polarimeter; it proved to be optically inactive. The hydrochloride of the base was also prepared; on examination in the polarimeter, it was found to be optically inactive.

From these results, it may be concluded that the *neo*-methylhydrindamine bromocamphorsulphonate is a partially racemic compound. Evidence of the homogeneous nature of the *dl-neo*-base in the bromocamphorsulphonate was obtained from an examination of the benzoyl derivative prepared by the Schotten-Baumann method. The crude substance, when washed and dried, melted at  $168^{\circ}$ , and recrystallisation failed to raise its melting point above  $169^{\circ}$ . From alcohol, it crystallises in glistening needles. It is insoluble in water, ether, and ligroin, and only moderately soluble in warm alcohol, warm benzene, warm acetone and cold ethyl acetate, but readily so in chloroform.

*Derivatives of dl-neo-Methylhydrindamine.*

The *hydrochloride* is similar to that of the isomeric base, but much less soluble. It crystallises from water in shining needles, and does not melt, but decomposes from  $235^{\circ}$  onwards.

The *normal sulphate* crystallises from water in transparent, irregular, hexagonal plates; its melting and decomposing point is about  $220^{\circ}$ .



The *picrate* prepared by precipitation is very sparingly soluble in water and crystallises from alcohol in yellow plates, which may approach the form of needles; it melts at 195—196°.

*Resolution of dl-Methylhydrindamine d-Bromocamphorsulphonate.*

It seemed at first that the resolution of the *dl*-methylhydrindamine into its enantiomorphously related components by using *d*-bromocamphorsulphonic acid would be impossible, since a very exhaustive process of fractional crystallisation is required in order to separate this partially racemic salt from the corresponding salt of *dl*-*neo*-methylhydrindamine. Subsequent investigation, however, showed that this salt, like the hydrindamine compounds, possessed a transition temperature somewhere between 30° and 70°, and that suitable treatment led to its resolution. To bring this about the salt, which has been rendered anhydrous by heating at 100°, is dissolved in absolute alcohol, and the solution concentrated until it becomes syrupy. A small quantity of hot ethyl acetate is then added, and the mixture well stirred; about 8 c.c. of the solvent are sufficient for 20 grams of salt. In a short time, a precipitate begins to form, and when about 1/10th to 1/5th of the salt has separated, the solution is quickly filtered through a heated funnel. It is generally necessary and always advantageous to treat the precipitate once more in the same way as the original substance, but the second filtrate should be kept separate from the first one.

The salt thus precipitated is that of the *l*-base; it is easily freed from partially racemic salt by crystallisation from water.

The ethyl acetate mother liquors may deposit needles of the *l*-component, or of the *d*-component, or thin prisms of the partially racemic salt, according to the proportion of the *l*-component which has already been separated, so that it occasionally happens that the deposits from the first and second filtrates, although indistinguishable in appearance, even after recrystallisation from water, really consist of the salts of the *l*- and *d*-bases respectively. For this reason, melting point determinations must always be made before mixing together deposits which are apparently identical. The recovered partially racemic compound is again treated as the original substance and finally the greater proportion of it is resolved into two salts, one of which, when crystallised from water, has an original melting point of 230°, and which we have called the *l*-component, the other, or *d*-component, having an original melting point of 249°.

*l-Methylhydrindamine d-Bromocamphorsulphonate.*

This salt crystallises from water in long, fine needles which are anhydrous; if allowed to crystallise by spontaneous evaporation of the solvent, it is obtained in prisms. It is readily soluble in hot water, alcohol, and chloroform, moderately so in cold water, and practically insoluble in ethyl acetate, ether, and light petroleum.

The salt originally obtained was crystallised sufficiently to ensure its freedom from any of the partially racemic salt, the presence of which is easily detected from its dissimilarity in crystalline form. Its melting point was 230°, and although softening occurred at 228° it seemed to be a pure single substance.

The specific rotation of this *l*-component was determined in aqueous and chloroform solutions. The salt was dried at 100°, and a different portion of the same sample was used for each experiment.

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| 0.4008       | Water      | 25 c.c.           | +1.47°       | +45.9°         | +210.2°   |
| 0.3977       | "          | 25 "              | 1.45         | 45.5           | 208.3     |
| 0.2080       | "          | 25 "              | 0.76         | 45.8           | 209.7     |
| 0.2757       | Chloroform | 20 "              | 0.54         | 19.5           | 89.3      |
| 0.2964       | "          | 20 "              | 0.54         | 18.2           | 83.3      |

The values for the molecular rotation of the salt in water indicate that it contains the *lævo*-component of the base. This was proved to be the case by decomposing a portion of the salt with barium hydroxide and distilling the base in steam; when brought into solution by the addition of alcohol and examined in the polarimeter, the base gave a very appreciable negative rotation.

*l-Methylhydrindamine Hydrochloride.*

The hydrochloride of *l*-methylhydrindamine is dimorphous; it crystallises from concentrated aqueous solutions in opaque, shining needles, which apparently occupy the whole bulk of the solution; these crystals, however, slowly change into either transparent or translucent, tabular crystals, which, in extreme cases of development, appear to be prisms, or into aggregations of transparent needles; in the latter forms, the substance does not occupy the whole bulk of the solution. The salt separates from a moderately concentrated solution in water, in which solvent it is readily soluble, in transparent needles.

The hydrochloride is moderately soluble in hot ethyl alcohol; when crystallised by spontaneous evaporation of the solvent, it is obtained in transparent, tabular crystals.

The specific rotation was determined with different samples dried at 100°:

| Wt. of salt. | Solvent. | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|----------|-------------------|--------------|----------------|-----------|
| 0.3622       | Water    | 20 c.c.           | -1.11°       | -30.3°         | -55.4°    |
| 0.1854       | "        | 20 "              | 0.57         | 30.7           | 56.1      |
| 0.7290       | "        | 20 "              | 2.28         | 31.2           | 57.0      |

*d*-Methylhydrindamine *d*-Bromocamphorsulphonate.

This salt is left in the filtrate obtained in the resolution of the partially racemic compound, and when present in large proportion it separates in rosettes of needles. It crystallises from water in long needles, somewhat thicker than those of the isomeric *l*-component, and is anhydrous. It is readily soluble in hot water, alcohol, and chloroform, moderately so in cold water, and practically insoluble in ethyl acetate. The salt originally obtained, when freed from the partially racemic compound, has a melting point of about 249°.

Like the *l*-component, from which it is indistinguishable by inspection, it has the outward characteristics of a pure single substance.

The specific rotations of this *d*-component were determined in aqueous and in chloroform solutions. A different sample was employed in each experiment, and all were dried at 100°:

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| 0.2995       | Water      | 20 c.c.           | +2.14°       | +71.4°         | +327.0°   |
| 0.2536       | "          | 20 "              | 1.80         | 70.9           | 324.7     |
| 0.2316       | Chloroform | 20 "              | 1.51         | 65.2           | 298.8     |

Judging from the values of the molecular rotation in dilute aqueous solution, this salt contains the *d*-base and this view was confirmed by liberating the base and examining its solution in aqueous alcohol in the polarimeter, when a large positive rotation was obtained.

*Regeneration of the partially Racemic Methylhydrindamine and neo-Methylhydrindamine Bromocamphorsulphonates.*

Up to this stage of the investigation, we had obtained no evidence of the existence of isomeric partially racemic salts derived from *dl*-methylhydrindamine or from the corresponding *neo*-base, and yet the close relationship between these bases and their lower homologue, hydrindamine, seemed to suggest the probable occurrence of a similar type of isomerism; it was, moreover, not unlikely that isomerides, other than those already isolated, might be present in the original mixture of *dl*-methylhydrindamine and *dl*-*neo*-methylhydrindamine bromocamphorsulphonates, although these might have remained undetected in



the residues which are left after separating the two salts just mentioned. Considering that, in the case of the hydrindamine compounds, the partially racemic  $\beta$ -salts are formed in relatively small proportions, it appeared probable that the methylhydrindamine and *neo*-methylhydrindamine salts which we had isolated corresponded with the partially racemic  $\alpha$ -salt of hydrindamine and that the  $\beta$ -forms had yet to be discovered. The best way of deciding this question seemed to be to decompose each of the pure partially racemic salts separately and regenerate it from its components; if  $\alpha$ - and  $\beta$ -salts were then produced the latter would no doubt be obtainable by fractionally crystallising the product which would, of course, be free from salts of the other externally compensated base.

These experiments were made, but in both cases the regenerated salt was, so far as we could ascertain, identical with the original compound, and was not resolved into different substances by fractional crystallisation; the bromocamphorsulphonate of the *dl-neo*-base crystallised so well that an isomeride if present and separable from it could hardly have escaped detection.

These results showed that the bromocamphorsulphonates of methylhydrindamine and *neo*-methylhydrindamine, when prepared under ordinary conditions, do not exist in separable isomeric partially racemic  $\alpha$ - and  $\beta$ -forms.

*Regeneration of l-Methylhydrindamine d-Bromocamphorsulphonate.  
Formation of the  $\alpha l$ - and  $\beta l$ -Isomerides.*

The last alternative to be considered before giving up the search for isomeric salts of the type  $NR_1R_2H_3$ , was the possibility that the partially racemic methylhydrindamine and *neo*-methylhydrindamine compounds might correspond with the partially racemic  $\beta$ -salts of hydrindamine and consist of the four isomerides *ad*, *al*,  *$\beta d$* , and  *$\beta l$* ; it is true that the characteristics of the two components obtained by the resolution of the methylhydrindamine compound did not accord well with the view that each is composite, but here again, considering the numerous crystallisations which are necessary in order to isolate the *l*- and *d*-components, the isomeric salts of the *l*- and *d*-bases might have remained undetected in the mother liquors or residues. If this were the case, the *l*-component, when decomposed and regenerated, should give a mixture of the  *$\alpha l$* - and  *$\beta l$* -forms, and should therefore be changed; similarly with the *d*-component, which should give a mixture of the  *$\alpha d$* - and  *$\beta d$* -salts. The experiment was tried first with the *l*-component in the following manner.

About 12 grams of the salt which by crystallisation had been freed entirely from the partially racemic compound was decomposed with barium

hydroxide, the base distilled in steam, and the acid recovered from the residu in the flask; the base and acid were then recombined, the solution concentrated, the product fractionally crystallised from water, and separated into eight fractions. Systematic fractionation was then continued, the mother liquors from the first deposit being used to dissolve the next, and so on. The final liquors (from fraction VII) were continually concentrated, whilst the first fraction was repeatedly crystallised from fresh water. At the commencement of these operations, the melting point of the first deposit was  $230^{\circ}$ , but after it had been crystallised about 30 times, its melting point rose to  $236^{\circ}$ . The melting points of the seven fractions were not quite sharp; they softened through a range of about  $3^{\circ}$ , and complete fusion took place when their temperatures were respectively  $236^{\circ}$ ,  $236^{\circ}$ ,  $235^{\circ}$ ,  $234^{\circ}$ ,  $232^{\circ}$ ,  $231^{\circ}$ , and  $230^{\circ}$ . Although the melting point of the first fraction was now  $6^{\circ}$  higher than that of the original material, and the first and last fractions differed in melting point by  $6^{\circ}$ , practically no difference in appearance could be detected between the first and last fractions, both crystallising in slender needles.

The first and last fractions were now separated, dried at  $100^{\circ}$ , and examined in the polarimeter, with the following results:

*First Fraction.*

|     | Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|-----|--------------|------------|-------------------|--------------|----------------|-----------|
| I   | 0.5037       | Water      | 25 c.c.           | +1.92°       | +47.6°         | +218.0°   |
| II  | 0.5043       | "          | "                 | 1.89         | 46.9           | 214.0     |
| III | 0.3965       | "          | 20 c.c.           | 1.86         | 47.0           | 215.2     |
|     | 0.4096       | "          | "                 | 1.95         | 47.6           | 218.0     |
| I   | 0.5037       | Chloroform | 25 c.c.           | 0.62         | 15.3           | 70.0      |
| II  | 0.5043       | "          | "                 | 0.72         | 17.9           | 82.9      |
| III | 0.3423       | "          | "                 | 0.52         | 19.0           | 87.0      |

The samples marked I and II were different samples of salt. After being used, these were placed together, crystallised from the mother liquors from which they had been separated, and used over again in the samples marked III:

*Last Fraction.*

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| 0.4057       | Water      | 25 c.c.           | +1.43°       | +44.0°         | +201.5°   |
| 0.3684       | "          | "                 | 1.32         | 44.8           | 205.1     |
| 0.3229       | "          | 20 c.c.           | 1.41         | 43.8           | 200.6     |
| 0.2080       | Chloroform | "                 | 0.37         | 17.8           | 81.5      |
| 0.5000       | "          | 25 c.c.           | 0.62         | 18.0           | 82.4      |
| 0.4057       | "          | "                 | 0.61         | 18.8           | 86.1      |

Owing to lack of material, these determinations had to be made with the same sample which, after being used, was recrystallised from the original mother liquors.

In order to obtain, if possible, a lower specific rotation for the last fraction than that given above, the last portions of the regenerated salt obtained in three separate experiments were mixed and crystallised systematically; the last fraction obtained by this means was separated, and when dried at 100°, it melted at 215—224°. Its specific rotation was determined in aqueous solution:

| Wt. of salt. | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|-------------------|--------------|----------------|-----------|
| 0.3480       | 20 c.c.           | +1.42°       | +40.8°         | +186.8°   |

These results show that whilst the rotations of the first and last fractions are approximately the same in chloroform, there is an appreciable difference in the values obtained with aqueous solutions. That the difference in rotation and melting point is not due to any unaltered partially racemic salt is certain, since the long and careful crystallisation to which the salt was subjected could not have failed to reveal its presence. The possibility of any ordinary impurity being present in the last fraction need hardly be considered, but it may be mentioned that these fractions were always carefully tested. As the acid used for the preparation of the regenerated salt was that recovered from the original salt, there is no question of the presence of the isomeric *l*-acid.

*Regeneration of d-Methylhydrindamine d-Bromocamphorsulphonate.  
Formation of  $\alpha d$ - and  $\beta d$ -Isomerides.*

The *d*-component, carefully freed from partially racemic salt, was decomposed and regenerated as in the case of the *l*-component. After prolonged systematic fractionation from water, carried out as described in the preceding experiment, the first fraction melted at 262°. The next fractions did not melt sharply, but softened through a few degrees, and were completely fused at the following temperatures respectively, 262°, 260°, 258°, 257°, 256°, 255°, and 254°. No difference in crystalline form could be detected, all fractions separating in needles.

The first and last fractions were separated, dried at 100°, and then examined polarimetrically.



*First Fraction.*

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| I 0.3642     | Water      | 20 c.c.           | + 2.64°      | + 72.5°        | + 332.0°  |
| II 0.3960    | "          | 20 "              | 2.96         | 74.7           | 342.1     |
| III 0.3798   | "          | 20 "              | 2.78         | 73.1           | 334.7     |
| I 0.3642     | Chloroform | 20 "              | 2.45         | 67.3           | 308.2     |
| II 0.3960    | "          | 20 "              | 2.69         | 67.9           | 310.9     |

I, II, and III were different portions of the same sample of material.

*Last Fraction.*

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| I 0.3946     | Water      | 20 c.c.           | + 2.70°      | 68.5°          | + 313.7°  |
| II 0.3835    | "          | 20 "              | 2.65         | 69.1           | 316.4     |
| III 0.3362   | "          | 20 "              | 2.31         | 68.7           | 314.6     |
| I 0.3946     | Chloroform | 25 "              | 2.54         | 64.4           | 294.9     |
| II 0.3835    | "          | 20 "              | 2.58         | 67.3           | 308.2     |
| III 0.3362   | "          | 20 "              | 2.21         | 65.7           | 300.9     |

Owing to the small quantity of substance obtainable the determination marked I, II, and III were made with practically the same sample of salt. After use in each experiment, it was recrystallised from the original mother liquors.

In order to obtain, if possible, a lower specific rotation for the last fraction than that recorded above, a mixture of the last fractions obtained in two separate experiments was fractionally crystallised; the last fraction, when dried at 100°, melted at 230—240°. Its specific rotation was determined in aqueous solution :

| Wt. of salt. | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|-------------------|--------------|----------------|-----------|
| 0.3677       | 20 c.c.           | + 2.47°      | + 67.1°        | + 307.3   |

From these results it is again evident that the first and last fractions are not the same; the melting point of the fractions is also higher than that of the original *l*-component obtained by the resolution of the partially racemic salt. For reasons similar to those given in considering the isomerism of the products of regeneration of the *l*-component, these facts cannot be ascribed to anything except the existence of isomeric *ad*- and *bd*-salts.

*Result of Mixing Equal Quantities of ad- and al-Salts.*

If the above conclusions be well founded and the *l*- and *d*-components are mixtures, whilst the first fractions of the regenerated

salts are pure substances, then the two latter when mixed should give a partially racemic salt differing from that already described (p. 926). To test this view, 0.17 gram of the first fraction of each of the regenerated salts was weighed out, and the specific rotation was then determined in chloroform and in water:

| Wt. of salt. | Solvent.   | Vol. of solution. | $\alpha_D$ . | $[\alpha]_D$ . | $[M]_D$ . |
|--------------|------------|-------------------|--------------|----------------|-----------|
| 0.34         | Chloroform | 20 c.c.           | +1.67°       | +49.1°         | +224.8°   |
| 0.34         | Water      | 20 „              | +2.05        | +60.3          | +276.1    |

The solution of the mixed salts was then evaporated and allowed to crystallise when it separated in hydrated, rectangular prisms. The melting point of the substance was 206°. An analysis of the dehydrated salt was made:

0.1963 gave 0.0793 AgBr. Br = 17.2.

$C_{10}H_{14}OBr \cdot SO_3H, C_{10}H_{13}N$  requires Br = 17.4 per cent.

The following data show the difference between this partially racemic salt and the original one:

|                     | Crystalline form.  | Melting point. | $[\alpha]_D$ in water. |
|---------------------|--------------------|----------------|------------------------|
| Original salt ..... | Oblique prisms     | 160—165°       | +51°                   |
| Synthetical salt... | Rectangular prisms | 206°           | +60                    |

These two salts, therefore, are obviously different substances, and it is equally obvious that the original partially racemic compound contains substances other than those representing the *first fractions* of the regenerated *l*- and *d*-components. The regenerated *l*- and *d*-components, as a whole, however, are practically identical with the *l*- and *d*-components as obtained by the resolution of the partially racemic salt; on mixing equal quantities of the latter before subjecting them to any systematic and prolonged crystallisation the original partially racemic salt is obtained.

*Result of Mixing Equal Quantities of the Last Fractions of the Regenerated d- and l-Methylhydrindamine Bromocamphorsulphonates.*

According to the foregoing conclusions, the last fractions of the regenerated *d*- and *l*-methylhydrindamine bromocamphorsulphonates consist of mixtures of isomeric  $\alpha d$ - and  $\beta d$ -salts, and  $\alpha l$ - and  $\beta l$ -salts respectively. By mixing equal quantities of these fractions, it was expected that a different synthetical partially di-racemic salt would be produced from that obtained by mixing the first fractions.

0.20 gram of the last fraction of the salt of the *d*-base ( $[\alpha]_D + 67.1^\circ$ ) was mixed with 0.20 gram of the last fraction of the salt of the *l*-base

$([\alpha]_D + 40.8^\circ)$  and the mixture was examined polarimetrically in aqueous solution:

| Wt. of salt. | Vol. of solution. | $\alpha_D$    | $[\alpha]_D$  | $[M]_D$        |
|--------------|-------------------|---------------|---------------|----------------|
| 0.40         | 20 c.c.           | $+2.15^\circ$ | $+53.7^\circ$ | $+245.9^\circ$ |

The solution was evaporated and the salt allowed to crystallise; it separated in hydrated rhomboidal prisms, which, when dehydrated, melted at  $157-160^\circ$ .

A sample of the salt was dried in the air until constant in weight and then dehydrated at  $100^\circ$ :

0.2975 lost 0.0093.  $H_2O = 3.1$  per cent.

It is evident that this synthetical salt is entirely different from the one (p. 936) obtained by mixing the first fractions.

The bromine was estimated in a sample of the salt which was dehydrated at  $100^\circ$ :

0.2027 gave 0.0824 AgBr. Br = 17.3

$C_{10}H_{13}N, C_{10}H_{14}OBr \cdot SO_3H$  requires Br = 17.4 per cent.

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## XCI.—Isomeric Compounds of the Type $NR_1R_2H_3$ .

By FREDERIC STANLEY KIPPING.

It has been shown in the preceding papers:—(1) that four isomeric salts are produced from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid of which three (*ad*, *al*, and *bl*) have been isolated in a pure state; (2) that *dl*-hydrindamine and *d*-chlorocamphorsulphonic acid yield four strictly analogous isomerides, all of which (*ad*, *bd*, *al*, *bl*) have been obtained in a pure condition; (3) that one of the two *dl*-methylhydrindamines combines with *d*-bromocamphorsulphonic acid, giving rise to four similar isomerides, but that in this case the  $\alpha$ - and  $\beta$ -compounds are so closely related that they cannot be completely separated, and only two of them (*ad* and *al*) have been isolated.

Further, it has been found that the salts formed from *d*- and *l*-hydrindamines with *cis*- $\pi$ -camphanic acid are different from the isomeric partially racemic  $\alpha$ - and  $\beta$ -salts previously described (Kipping,



Trans., 1900, 77, 861), and that each probably consists of two isomerides corresponding with those of the bromo- and chloro-camphor-sulphonic acids.

Finally, in conjunction with Mr. Tutin, the author has commenced the study of salts of menthylamine, and here also there is distinct evidence that the pure optically active base gives with *d*-bromocamphorsulphonic acid a mixture of two salts.

Since of the four isomerides produced from a *dl*-base two are derived from the *d*- and two from the *l*-component, the former may be distinguished as the *ad*- and *βd*-, the latter as the *al*- and *βl*-salts; and should these four isomerides unite in pairs or otherwise to form two partially racemic salts, as in the case of the hydrindamine compounds, the latter may be classed as *α*- and *β*-salts according as to whether they contain the *ad*- and *al*-, or the *βd*- and *βl*-isomerides; the salts produced in relatively smaller quantities may be classed as *β*-salts, or salts of the *β*-series.

It is proposed to discuss in this paper the nature of these isomerides, and to consider what conclusions may be drawn from their existence.

In the first place, it is perhaps desirable to examine critically the explanation which the author has previously given of the existence of such isomerides. An obvious question which then arises, and on the answer to which the given explanation depends, is, are these substances, in fact, *isomeric salts*?

The evidence on this point is as follows:—(1) the results of analyses (halogen determinations) of the partially racemic hydrindamine bromocamphorsulphonates and chlorocamphorsulphonates (Trans., 1900, 77, 874 and 891); (2) determinations of the percentage of base in the partially racemic *cis*- $\pi$ -camphanates (*loc. cit.*, pp. 906—907); (3) an analysis of the *βl*-isomeride of hydrindamine *d*-bromocamphorsulphonate.

It would seem on theoretical grounds that the only possible difference in composition between a salt of the *α*- and a salt of the *β*-series would be the elements of one molecule of water, but on theoretical grounds also it is almost impossible that such a difference could exist; as analyses would fail to conclusively establish such a difference in composition, the proof that the substances are isomeric rests chiefly on the proof that they are *salts*.

This is established by the behaviour of the isomerides towards reagents, such as sodium carbonate and barium hydroxide, which immediately liberate the base; hydrochloric acid, which liberates the organic acid; picric acid, which gives a picrate of the base, and platinichloric acid, which precipitates a platinichloride. Further, molecular weight determinations show that the isomerides undergo

ionic dissociation to a very considerable extent, and corresponding isomerides have the same or practically the same solubility in cold water.

The next question which arises, and one which is intimately connected with the foregoing, is, do the salts of the  $\alpha$ -series consist of identically the same components as those of the  $\beta$ -series, or is the difference between them due to the existence of structurally or optically isomeric acids or bases?

This question seems to be settled beyond all doubt by many and by very different pieces of evidence. The *ad*- and  *$\beta$ d*-isomerides are salts of the same acid and the same base, because when the *ad*-salt is decomposed and regenerated from its components it gives some  *$\beta$ d*-salt; similarly, the *al*-derivative gives some  *$\beta$ l*-salt, and neither the acid nor the base undergoes structural change or racemisation during the decomposition and regeneration. Further, the partially racemic  $\beta$ -salts can be transformed into the  $\alpha$ -salts by repeatedly evaporating with *dl*-base (*loc. cit.*, pp. 882, 897, 907); this treatment could hardly bring about any change in the acid or in the percentage composition of the salt. It has also been proved by independent experiments that the acid from the partially racemic  $\beta$ -salts is identical optically with that of the  $\alpha$ -isomerides (*loc. cit.*, p. 877).

The possibility of the existence of isomeric hydrindamines, other than the *d*- and *l*-bases indicated by theory, has previously been discussed and shown to be out of the question (*loc. cit.*, p. 883); this conclusion is established beyond doubt by some of the experiments just mentioned and by others described below.

The striking similarity between the *ad*- and  *$\beta$ d*-isomerides, and between the *al*- and  *$\beta$ l*-isomerides, which sometimes extends to all their properties, apparently even to the existence of isodimorphism, can only be accounted for satisfactorily on the assumption that they are all salts, and the fact that the compounds are only separated with great difficulty, or cannot be separated, also affords strong confirmation of this view.

That the observed isomerism is not due to any peculiarity of the *d*-bromo- and *d*-chloro-camphorsulphonic acids seems to be proved conclusively by the existence of the *cis*- $\pi$ -camphanates, and by the fact that with some primary bases these acids do not yield separable isomerides; the existence of the derivatives of methylhydrindamine and of menthylamine shows also that the phenomena are not caused by some special characteristic of hydrindamine. From a consideration of all these facts, it may be concluded that the explanation originally given by the author (*loc. cit.*, p. 862) is the correct one; that is to say, the difference between the *ad*- and  *$\beta$ d*-salts and between the *al*- and  *$\beta$ l*-salts is



due to the acidic ion in the  $\beta$ -compounds being attached to a nitrogen valency which is differently situated from that which fixes the acid ion in the  $\alpha$ -isomerides.

If this explanation be accepted, it would seem that the acidic ion which is separated from the basic ion in dilute aqueous solution returns to its own particular nitrogen valency, to its original position in the molecule, when the salt is re-formed on concentrating the solution; otherwise either of the pure  $\alpha$ -isomerides, when dissolved in a sufficiently large quantity of water, would give, on evaporating, a mixture of certain fixed proportions of the  $\alpha d$ - and  $\beta d$ -salts and similarly pure  $\alpha l$ - or  $\beta l$ -salt would give a product consisting of both forms; experiment shows that this does not occur, all the isomerides being recovered unchanged after solution in water or other solvents (except in the case of the *cis*- $\pi$ -camphanates, which being dissociated hydrolytically, necessarily behave in a different manner, *loc. cit.*, p. 908). Consequently, it may be inferred that there are *two different ions* of each of the optically active bases.\*

Proceeding a step further, it seems reasonable to suppose that if the acidic ion of any one of the given salts be displaced by a different acidic ion, the latter should take up the same position in the molecule as that occupied by the former; in other words, a salt of the  $\beta d$ -series, for example, should be convertible into other salts of the same series without at the same time giving rise to an isomeride of the  $\alpha d$ -series, so long as the base is never set free.

An interesting set of experiments which tests the validity of this deduction may be readily carried out with the partially racemic  $\beta$ -salt of hydrindamine and *d*-bromocamphorsulphonic acid. When a dilute aqueous solution of this salt is treated with a solution of sodium carbonate, no visible effervescence is produced and the solution remains free from precipitated base; doubtless, however, some of the *d*-bromocamphorsulphonate is converted into carbonate (for, on warming, the base is evolved); if, however, the solution is immediately acidified with hydrochloric acid, carbon dioxide is expelled, and a certain proportion of the hydrindamine salt is no doubt converted into hydrochloride. On subsequently evaporating the solution to dryness and crystallising the residue from water, the  $\beta$ -salt separates unchanged and the deposit is free from the characteristic crystalline masses of the partially racemic  $\alpha$ -salt.

Although, therefore, a portion of the *d*- and *l*-bases have been in union with the ions of carbonic and of hydrochloric acids, the relative and absolute quantities of the four isomeric *d*-bromocamphorsulphonates in the recovered salt are the same as in the original sample, or

\* This conclusion, if correct, excludes the possibility of the isomerism being due to the limitation of free rotation (compare *loc. cit.*, p. 866).



at any rate appear to be so, for if the proportions of the *adl*- and *al*-isomerides had been increased to any appreciable extent, the excess would separate as partially racemic  $\alpha$ -salt.

If instead of acidifying with hydrochloric acid immediately, the solution of the partially racemic  $\beta$ -salt (to which sodium carbonate has been added) is left at the ordinary temperature during 24 hours and then acidified, it gives on subsequent evaporation a deposit of a mixture of both  $\alpha$ - and  $\beta$ -partially racemic salts and from this mixture the two isomerides can be easily isolated in the usual manner.

This difference in behaviour seems to be satisfactorily accounted for as follows: the carbonate of the base is no doubt dissociated hydrolytically, and during the 24 hours a large proportion, or the whole, of the base is for some short period in the free state; when the carbonic acid ions again unite with the free base a greater proportion of the *adl*- and *al*-isomerides is produced than was contained in the partially racemic  $\beta$ -salt; from these, the corresponding hydrochlorides, and finally the *d*-bromocamphorsulphonates are formed, and, on crystallising, the excess of the *adl*- and *al*-modifications separates as partially racemic  $\alpha$ -salt.

A similar result may of course be achieved much more quickly, for if the  $\beta$ -salt is decomposed with barium hydroxide solution, the base extracted with ether, and combined again with the *d*-bromo-acid, both  $\alpha$ - and  $\beta$ -salts are produced, and it is immaterial whether a fresh sample of the bromo-acid or that recovered from the solution of the barium salt be employed. If, on the other hand, the partially racemic  $\beta$ -salt is dissolved in excess of concentrated hydrochloric acid, the solution heated on the water-bath during several hours, and then repeatedly evaporated with water to expel the hydrochloric acid, the  $\beta$ -salt is finally recovered, free from the  $\alpha$ -isomeride; during these operations the base is never in the free state and the relative proportions of the four components of the  $\beta$ -salt remain unaltered.

Further experiments with the *adl*-, *al*-, and  $\beta$ *l*-hydrindamine *d*-bromocamphorsulphonates seem to confirm this conclusion, that one acidic ion may be displaced by another without changing the configuration particular to the salt.

In the first place, it may be mentioned that the pure *adl*-, *al*-, and  $\beta$ *l*-salts, when separately dissolved in water and treated with a solution of picric acid, give precipitates of *picrates*, which are identical in crystalline form, so far as can be ascertained without goniometrical examination, and which show the same behaviour when heated. This fact merely affords additional evidence that the three compounds are all salts, and that the bases of the three salts are identical, except as regards optical properties; since the *picrates* are probably dissociated

hydrolytically, it is to be presumed that all three precipitates are mixtures of salts of both the  $\alpha$ - and  $\beta$ -series.

When *ad*-, *al*-, and  $\beta$ *l*-hydriindamine *d*-bromocamphorsulphonates, which were chosen as suitable representatives of the  $\alpha$ - and  $\beta$ -series respectively, are treated with concentrated hydrochloric acid, they dissolve freely, much more readily than in water; on adding platinichloric acid to the solutions, the platinichlorides are obtained as bulky, yellow precipitates, but precipitation is only incomplete, owing to the presence of the bromo-acid. When separated and recrystallised from water, the three salts are obtained in crystals of characteristic appearance, which, so far as ordinary examination goes, are identical with one another and with those of the platinichlorides, which are prepared from the hydrochlorides of the *d*- and *l*-bases.

As a matter of fact, of course, the platinichlorides of the *ad*-, *al*-, and  $\beta$ *l*-salts cannot be identical in optical properties, and those of the *ad*- and *al*-isomerides bear the ordinary enantiomorphous relationship to one another; the question arises, what is the relationship of the salt prepared from the  $\beta$ *l*-form to that obtained from the *ad*-isomeride?

In order to gain further information on this matter, the platinichlorides from the *ad*- and  $\beta$ *l*-salts, prepared as just described, were separately dissolved in dilute hydrochloric acid and hydrogen sulphide passed through the warm solutions until precipitation was complete; the solutions of the hydrochlorides were then concentrated and allowed to crystallise slowly. They both deposited large, tabular, transparent crystals of characteristic appearance, apparently identical with one another and with the hydrochlorides obtained by neutralising the *d*- and *l*-bases with the acid; the apparent identity in outward properties extended to their melting points, the two hydrochlorides fusing simultaneously at about  $233^\circ$ .

It might be inferred from these statements that when the ions of the *d*-bromocamphorsulphonic acid in the *ad*- and  $\beta$ *l*-salts are displaced by those of an optically inactive acid, the resulting salts bear the ordinary enantiomorphous relationship to one another, and that, otherwise, there is no difference between a salt of the *ad*- and one of the  $\beta$ *l*-series. This, however, does not seem to be the case; there would appear to be some extremely subtle difference between the hydrochlorides of the *ad*- and  $\beta$ *l*-series, in addition to that determined by the enantiomorphous relationship of the bases, because, when the chlorine ion in each of the salts is displaced by that of the bromo-acid the original *ad*- or  $\beta$ *l*-isomeride, as the case may be, is obtained. This statement is based on experimental evidence which appears to be conclusive, but it is put forward here with a reservation, and further investigation will be made. The evidence is as follows:

In the first place, the partially racemic  $\beta$ -salt of the bromo-acid is



recovered unchanged after it has been heated with hydrochloric acid, a fact which seems to prove that each of its four isomeric components is converted into the *corresponding* hydrochloride, from which the *corresponding* bromo-salt is again formed; apparently, therefore, there are *four different hydrindamine hydrochlorides*.

Secondly, the  $\beta$ l-form of hydrindamine *d*-chlorocamphorsulphonate can be transformed into a hydrindamine hydrochloride, which, when treated with the chloro-acid again, yields the  $\beta$ l-chloro-salt; that is to say, this  $\beta$ l-chloro-salt, when digested with concentrated hydrochloric acid during 24 hours, is recovered unchanged on subsequently evaporating to dryness several times with water. The  $\beta$ l-chloro-salt was used in this experiment in preference to the  $\beta$ l-bromo-salt merely because it is easily distinguished from its *al*-isomeride by its melting point. The latter always melts below  $121^\circ$ , whereas the  $\beta$ l-compound never does so; the crystals obtained after treatment with hydrochloric acid melted at about  $140^\circ$ , and doubtless consisted of the pure  $\beta$ l-isomeride. This experiment has been made more than once, and in order to obtain ocular proof that the chloro-salt is actually transformed into its hydrochloride, the solution in hot concentrated hydrochloric acid was first left to crystallise at the ordinary temperature; the few crystals then deposited consisted of lustrous, transparent, rectangular prisms, indistinguishable in appearance and in melting point from the crystals of the other hydrochlorides; from these crystals, the  $\beta$ l-salt was obtained as described already.

Owing to the great solubility of the hydrochlorides, in comparison with that of the bromo- or chloro-camphorsulphonates, it is not easy to isolate more than a relatively small proportion of the salt of the mineral acid in one operation; as, moreover, the salts of the  $\beta$ -series are very troublesome to obtain, and are only available in small quantities, another method was tried for converting them into their hydrochlorides and back again into salts of organic acids.

The hydrochloride obtained from the  $\beta$ l-modification of hydrindamine bromocamphorsulphonate by precipitating as platinichloride and then decomposing with hydrogen sulphide (p. 942), was treated with ammonium *d*-bromocamphorsulphonate in aqueous solution, and the hydrindamine bromocamphorsulphonate thus precipitated was recrystallised from water; this product seemed to be identical with the original  $\beta$ l-salt in crystalline form, but, unfortunately, the quantity of the supposed  $\beta$ l-salt available was too small for a determination of its specific rotation, which was perhaps the only way in which it could with certainty be distinguished from its *al*-isomeride; a repetition of the experiment on a larger scale was therefore desirable.

Wishing to improve the yield of platinichloride, the  $\beta$ l-salt of the chloro-acid was dissolved in water and treated with hydrochloric acid



and sodium chloride, and then with platinic chloride; the precipitate was crystallised from *water*, and then from aqueous methyl alcohol, and finally decomposed with hydrogen sulphide in boiling solution; the hydrochloride, which was then obtained, was decomposed with ammonium *d*-bromocamphorsulphonate, the bromo-salt separated, washed with a small quantity of water, and dried.

0.4706 gram dissolved in water, the solution diluted to 25 c.c., and examined in a 200 mm. tube, gave  $\alpha_D + 2.28^\circ$  whence  $[\alpha]_D + 60.5^\circ$ .

The salt is therefore the *al*-isomeride, the specific rotation of the *bl*-compound being  $[\alpha]_D + 39^\circ$ .

Whether this result is due to the crystallisation of the platinic chloride from water instead of from hydrochloric acid, or to some intramolecular change, such as occurs in the case of the *d*- and *l*-methylethylphenacylthetine *d*-bromocamphorsulphonates when they are precipitated as mercurichlorides (Pope and Neville, *Trans.*, 1902, 81, 1559) has not yet been determined; whatever the cause may be, it would seem that the basic ion of the  $\beta$ -series may in some cases be transferred from one acidic ion to another without losing its own particular configuration; further experiments on this point will be made as soon as the necessary materials have been prepared.

#### *Molecular Rotations of the Isomeric Salts.*

The only fact arising out of these investigations which is not in complete harmony with the author's views regarding the nature of these isomerides is that some of the salts seem to have highly abnormal molecular rotations.

The isomerides of the  $\alpha$ -series have in all cases molecular rotations which in 2 per cent. aqueous solution approximate sufficiently closely to the calculated values, as shown in the following table:

|   | Basic ion.               | Acidic ion.   | Salt.         |               |
|---|--------------------------|---------------|---------------|---------------|
|   |                          |               | Observed.     | Calculated.   |
| <i>al</i> -Hydrindamine <i>d</i> -bromocamphorsulphonate .....    | $[\text{M}]_D - 1^\circ$ | $+ 270^\circ$ | $+ 271^\circ$ | $+ 269^\circ$ |
| <i>al</i> -Hydrindamine <i>d</i> -bromocamphorsulphonate ... ..   | „ $+ 1$                  | 270           | 267           | 271           |
| <i>al</i> -Hydrindamine <i>d</i> -chlorocamphorsulphonate .....   | „ $- 1$                  | 187           | 184           | 186           |
| <i>al</i> -Hydrindamine <i>d</i> -chlorocamphorsulphonate .....   | „ $+ 1$                  | 187           | 177           | 188           |
| <i>al</i> -Methylhydrindamine <i>d</i> -bromocamphorsulphonate .. | „ $+ 56$                 | 270           | 336           | 326           |
| <i>al</i> -Methylhydrindamine <i>d</i> -bromocamphorsulphonate .. | „ $- 56$                 | 270           | 216           | 214           |

It is to be observed, nevertheless, that in the case of the hydrindamine bromo- and chloro-camphorsulphonates, the *ad*-salts have slightly higher values than the *al*-isomerides, although the basic ion which they contain is levorotatory so far as can be determined by an examination of the hydrochloride of the base in moderately concentrated solutions.

The salts of the  $\beta$ -series, on the other hand, are highly abnormal in their optical properties, as shown in the following table:

|   |       |                       |        | Salt      |             |
|---|-------|-----------------------|--------|-----------|-------------|
|   |       |                       |        | Observed. | Calculated. |
| $\beta$ -l-Hydrindamine <i>d</i> -bromocamphorsulphonate* | ..... | [M] <sub>D</sub> - 1° | + 270° | + 222°    | + 269°      |
| $\beta$ -l-Hydrindamine <i>d</i> -bromocamphorsulphonate  | ..... | „ + 1                 | 270    | 178       | 271         |
| $\beta$ -l-Hydrindamine <i>d</i> -chlorocamphorsulphonate | ..... | „ - 1                 | 187    | 236       | 186         |
| $\beta$ -l-Hydrindamine <i>d</i> -chlorocamphorsulphonate | ..... | „ + 1                 | 187    | 230       | 188         |

\* Impure salt.

The methylhydrindamine bromocamphorsulphonates of the  $\beta$ -series were not obtained sufficiently free from their  $\alpha$ -isomerides to give values which can be regarded as even approximately correct, but as the impure preparations have molecular rotations considerably lower than those of the  $\alpha$ -salts, the pure compounds would doubtless give results comparable with those obtained from the hydrindamine bromo-salts of the  $\beta$ -series.

What is the explanation of these apparently abnormal values?

In the case of the bromo-salts, the observed are very much lower than the calculated values; in that of the chloro-salts, the contrary is the case. Assuming, then, that the salts of the two acids are ionised to an approximately equal extent, it is manifest that the abnormal values cannot be due to the ions of the *d*-acids; but the basic ions have no appreciable optical activity, judging from the examination of their hydrochlorides, so that the natural conclusion is that the abnormal values are due to incomplete ionic dissociation.

In order to obtain some knowledge of the relative extent of the ionic dissociation of the isomeric hydrindamine bromocamphorsulphonates, molecular weight determinations were made in aqueous solution by the ebullioscopic method, using the modified apparatus devised by Landsberger; in the first place, the partially racemic  $\alpha$ - and  $\beta$ -salts were used, and the results, which are given below, may be compared with some previous determinations made in aqueous solution by the cryoscopic method.

*Partially Racemic  $\alpha$ -Salt.**Cryoscopic method.*

| Substance. | Water.   | Percentage of salt. | D.    | Mol. weight. |
|------------|----------|---------------------|-------|--------------|
| 0.2 gram   | 25 grams | 0.8                 | 0.075 | 203          |
| 0.2 „      | 25 „     | 0.8                 | 0.067 | 227          |

*Ebullioscopic method.*

|     |          |            |      |        |     |
|-----|----------|------------|------|--------|-----|
|     | 1.0 gram | 24.5 c.c.* | 4.08 | 0.100† | 212 |
|     | 1.0 „    | 23.0 „     | 4.3  | 0.090  | 246 |
|     | 1.0 „    | 20.0 „     | 5.0  | 0.130  | 200 |
| (a) | 1.0 „    | 17.0 „     | 5.9  | 0.094  | 320 |
|     | 1.0 „    | 17.0 „     | 5.9  | 0.116  | 269 |
|     | 1.0 „    | 16.0 „     | 6.2  | 0.140  | 230 |
|     | 1.0 „    | 14.0 „     | 7.1  | 0.140  | 264 |
|     | 1.5 „    | 21.0 „     | 7.1  | 0.152  | 248 |
|     | 1.0 „    | 12.0 „     | 8.3  | 0.140  | 296 |
|     | 1.5 „    | 18.0 „     | 8.3  | 0.130  | 332 |
|     | 2.0 „    | 22.0 „     | 9.1  | 0.164  | 290 |
|     | 1.5 „    | 16.0 „     | 9.4  | 0.170  | 287 |
|     | 1.5 „    | 17.0 „     | 9.4  | 0.130  | 360 |
| (b) | 2.0 „    | 21.0 „     | 10.0 | 0.190  | 260 |
|     | 1.5 „    | 14.5 „     | 10.3 | 0.140  | 382 |
|     | 1.5 „    | 11.5 „     | 13.0 | 0.218  | 310 |
|     | 1.5 „    | 10.5 „     | 14.2 | 0.210  | 351 |

\* Volume of solution.

† E.

With regard to these results, it may be stated that in order to give some idea as to the reliance which may be placed on them no selection has been made, and consequently some data, as, for example, those of experiments (a) and (b), which might be attributed to fortuitous errors, have not been omitted. As comparative values only were required, the volume of the solution at the ordinary temperature was taken to represent the weight of the solvent.

Although the results are not very satisfactory, owing to the large experimental error, they seem to show that ionic dissociation diminishes very rapidly with increasing concentration; taking the mean values, the following relation is observed:

|                    |     |         |         |         |
|--------------------|-----|---------|---------|---------|
| Percentage of salt | 0—5 | 5.9—7.1 | 8.3—9.4 | 10—14.2 |
| M. W. ....         | 219 | 266     | 313     | 326     |

Assuming that the results in 0—5 per cent. solution afford a true indication of the extent of ionic dissociation, it may be further con-



cluded that in such solutions the  $\alpha$ -*l*- and  $\alpha$ -*l*-isomerides are completely ionised, the molecular weight of the salt being 444.

The partially racemic  $\beta$ -salt was next examined, with the following results :

*Cryoscopic method.*

| Substance. | Water.   | Percentage<br>of salt. | <i>D</i> . | Mol. weight. |
|------------|----------|------------------------|------------|--------------|
| 0.3 gram   | 25 grams | 1.2                    | 0.100      | 228          |
| 0.2 "      | 25 "     | 0.8                    | 0.065      | 234          |
| 0.3 "      | 25 "     | 1.2                    | 0.090      | 235          |

*Ebullioscopic method.*

|       |          |      |        |     |
|-------|----------|------|--------|-----|
| 0.5 " | 15 c.c.* | 3.3  | 0.055† | 312 |
| 1.0 " | 16 "     | 6.2  | 0.120  | 269 |
| 1.0 " | 15.5 "   | 6.4  | 0.110  | 311 |
| 1.0 " | 10.5 "   | 9.5  | 0.157  | 314 |
| 1.5 " | 15 "     | 10.0 | 0.167  | 311 |
| 1.0 " | 10 "     | 10.0 | 0.160  | 352 |

\* Volume of solution.

† *E*.

Comparing these with the results obtained in the case of the  $\alpha$ -salt, the inference may be drawn that in dilute (0—7 per cent.) solutions the  $\beta$ -salt is not so fully dissociated as its  $\alpha$ -isomeride.

Now, since two of the components of the  $\beta$ -salt are identical, respectively, with the two components of the  $\alpha$ -salt, it seemed probable that the higher values obtained with the former must be due to the  $\beta$ -*l*- and  $\beta$ -*l*-isomerides, and that the latter would therefore give even higher values than the partially racemic  $\beta$ -salt; a comparison was therefore made between the  $\alpha$ -*l*- and  $\beta$ -*l*-isomerides, with the following results :

*$\alpha$ -Salt.*

| Substance. | Water.  | Percentage of<br>salt. | <i>E</i> . | Mol. weight. |
|------------|---------|------------------------|------------|--------------|
| 1.0 gram   | 21 c.c. | 4.7                    | 0.111      | 220          |
| 1.0 "      | 15.5 "  | 6.4                    | 0.133      | 257          |
| 1.0 "      | 15.5 "  | 6.4                    | 0.125      | 265          |
| 1.0 "      | 15 "    | 6.6                    | 0.133      | 258          |
| 1.0 "      | 12 "    | 8.3                    | 0.135      | 320          |

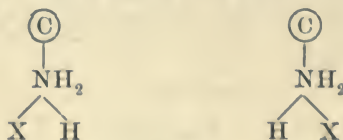
*$\beta$ -Salt.*

| Substance. | Water.  | Percentage of salt. | <i>E.</i> | Mol. weight. |
|------------|---------|---------------------|-----------|--------------|
| 0.65 gram  | 20 c.c. | 3.25                | 0.065     | 260          |
| 0.50 „     | 12.5 „  | 4.00                | 0.080     | 260          |
| 1.0 „      | 20 „    | 5.0                 | 0.083     | 313          |
| 1.0 „      | 19.0 „  | 5.3                 | 0.115     | 240          |
| 1.0 „      | 17.7 „  | 5.7                 | 0.100     | 296          |
| 1.15 „     | 16 „    | 7.0                 | 0.130     | 280          |
| 1.0 „      | 12 „    | 8.3                 | 0.146     | 295          |
| 1.5 „      | 15 „    | 10.0                | 0.180     | 290          |

The values thus obtained do not indicate any very great difference between the two salts in the degree of ionic dissociation, although in very dilute solutions they are perhaps lower in the case of the *α*- than in that of the *β*-isomeride; all the results tend to show, however, that ionisation is very incomplete in only moderately concentrated aqueous solutions at  $100^\circ$ ; whether it is less or greater at the ordinary temperature it is impossible to say, and consequently the experimental evidence in favour of the view that the abnormal molecular rotations of the *β*-salts are due to incomplete dissociation is not by any means conclusive.

*The supposed Relationship of the Isomerides.*

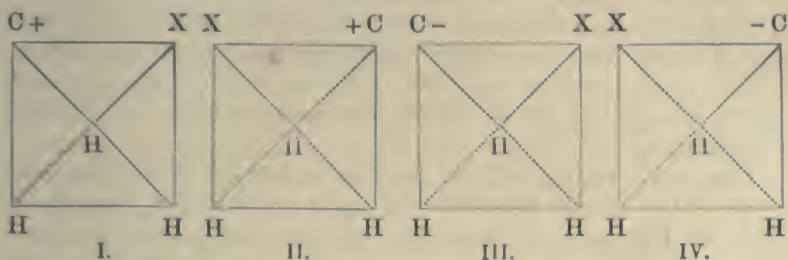
To account for the occurrence of such isomeric salts of the type  $\text{NR}_1\text{R}_2\text{H}_3$ , it is only necessary to assume (*a*) that when the optically active base combines with the acidic ions X and H each of the latter may take up one of two positions, giving the dissimilar forms :



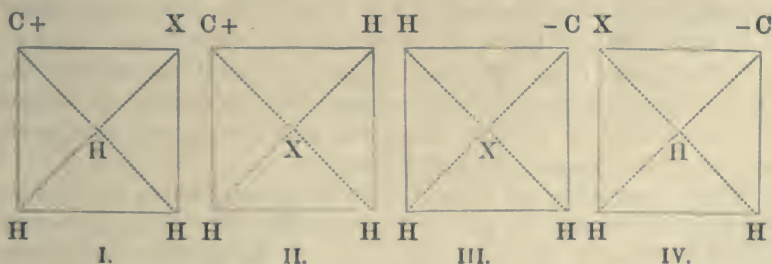
and (*b*) that the valencies which fix these ions are not so situated that the two groups become identical by free rotation; in other words, these valencies must not be in the same plane as, and at the same time symmetrically situated with regard to, the valency which unites the carbon and nitrogen atoms.

The double tetrahedron configuration for nitrogen, for example, would not account for such isomerism; the square pyramid configuration, however, would satisfy these conditions, and may be conveniently made use of to indicate the suggested relationship of the isomerides.

Assuming that the asymmetric carbon atom and the two hydrogen atoms of the amino-group are arranged symmetrically in one plane around the nitrogen atom, and that when the latter becomes quinquevalent the acidic ions arrange themselves in such a way that they lie in one plane with the carbon and one of the hydrogen atoms, then each of the optically active bases could give rise to two isomerides, the configurations of which would be represented as follows :



If, on the other hand, it be assumed that in the transformation of tri- into quinque-valent nitrogen, one of the three atoms of hydrogen originally in one plane with the nitrogen atom may change its position, but that otherwise the results are analogous, the four arrangements represented by the following symbols would be obtained :



It is not impossible, of course, that combination might result in the formation of all the above configurations, in which case there would be six isomerides produced, four of which might combine in pairs to produce the  $\alpha d$ - and  $\alpha l$ -salts, the other two representing the  $\beta d$ - and  $\beta l$ -salts, or *vice versa*.

Adopting either of these views, it will be seen that when the acidic ions X are removed there are left two pairs of enantiomorphously related basic ions, namely, I and IV, and II and III ; the basic ions of the four isomeric salts should, therefore, have two numerically different molecular rotations, namely,  $\pm x$  and  $\pm y$ ; in other words, the mean



of the molecular rotations of the  $\alpha d$ - and  $\alpha l$ -salts, and the mean of the molecular rotations of the  $\beta d$ - and  $\beta l$ -isomerides, if all are sufficiently dissociated, should be the same and also identical with that of the  $d$ -bromo-acid.

Experiment shows that this is not the case, and that all the  $\beta$ -isomerides have molecular rotations, which, judged by the usual criteria, are highly abnormal, those of the bromo-acid being much too low, those of the chloro-acid far too high; unless, therefore, optical activity is conditioned by the arrangement of the atoms and groups around the nitrogen atom, which hardly seems a reasonable supposition, it may be inferred, at any rate provisionally, that the abnormal optical behaviour of the salts of the  $\beta$ -series is due to incomplete ionic dissociation.

This view, that the salts of the  $\beta$ -series are less dissociated than those of the  $\alpha$ -series in solutions of equal concentration, is, perhaps, perfectly legitimate on theoretical grounds alone, since the compounds are stereochemically isomeric, and considerable differences between such compounds, as, for example, between the *cis*- and *trans*-forms of acids, are known to exist.

The question whether the existence of such isomerides as those described in these papers is a purely fortuitous circumstance or a general rule is no doubt one of considerable interest; as there seems to be no special reason why hydrindamine, methylhydrindamine, and benzylhydrindamine (compare *Trans.*, 1901, 79, 430) should differ from other nitrogen bases, and as, of the only other bases ( $d$ -phenylethylamine and  $l$ -menthylamine) which have yet been carefully examined menthylamine certainly affords such isomerides, the author concludes that all nitrogen bases may give rise to two salts corresponding with those of the  $\alpha$ - and  $\beta$ -series.

When these salts are derived from an optically active base and an optically active acid, the isomerides may differ in properties to a very considerable extent, as in the case of  $\alpha d$ - and  $\beta d$ -hydrindamine chlorocamphorsulphonates, or they may be so closely similar as to be barely separable, as in the case of the methylhydrindamine bromocamphorsulphonates, or they may show an intermediate behaviour; when, however, only the acid or the base is optically active, the isomerides may exhibit a great similarity, and probably be inseparable, and, possibly, indistinguishable as such. When, finally, both acid and base are optically inactive, the isomerides, which might be related as object and mirror image, would probably be indistinguishable and inseparable.

The objection that isomerides such as those of the first group must, if existing, have been discovered before, has little, if any, weight; it is very doubtful whether many such salts have been submitted to the

prolonged crystallisation which would be necessary to effect their separation, and unless the presence of such isomerides was expected, they would certainly escape detection; the formation of two isomeric partially racemic salts from such acids and bases, which might have led to the discovery of isomerides of the type  $NR_1R_2H_3$ , is possibly a rare occurrence; lastly, it must be borne in mind that such isomerides cannot be separated by crystallising from water or aqueous alcohol if they undergo hydrolytic dissociation to any extent, because the more soluble would be transformed into the less soluble modification.

The great stability of the isomeric bromo- and chloro-camphor sulphonates, and the fact that the  $\beta$ -salts are not transformed into the  $\alpha$ -forms, or *vice versa*, in aqueous solution, is perhaps at first sight contrary to preconceived notions, but so far as the author is aware, there are no known facts which point to instability in the molecular configuration of an ion.

Leaving these salts, it is of course obvious that isomerism should be observed in the case of other derivatives of quinquivalent nitrogen. In addition to that of the optically active compounds which have been isolated by Pope and Peachey (*Trans.*, 1899, 75, 1127), the only other case which need be considered here is that of the isomeric optically inactive phenylbenzylallylmethylammonium iodides described by Wedekind.

In his last paper (*Ber.*, 1903, 33, 1158), Wedekind comes to the conclusion that quaternary ammonium salts containing one asymmetric nitrogen atom, that is to say, salts of the type  $NR_1R_2R_3R_4R_5$ , exist in general in only one optically inactive form, and refers to the isomerism of the phenylbenzylallylmethylammonium salts as being "noch ein Räthsel."

This conclusion, apparently, is not based on theoretical grounds, but on the negative results of a number of experiments which were carried out on the same lines as those which previously resulted in the actual discovery of isomerides; it is not very clear, therefore, why conclusions drawn from negative results, although these may be more numerous, should be preferred to those based on positive ones.

In experiments such as those of Wedekind, everything depends on the stability and solubility of the quaternary compounds; it seems to be not impossible that a tertiary base, NABC, may combine with an alkyl iodide, giving two salts which may be enantiomorphously related, namely, NABCXY and NABCYX, and similarly a base, NABX, may give NABXCY and NABXCO; of these, one pair, say the latter, is more stable, or, if both be unstable, less soluble, than the other one; the former, in solution, undergoes partial dissociation, giving NABX and CY, which recombine to form the latter as crystallisation takes

place. If, of course, both the quaternary salts, NABX<sub>2</sub>Y and NABXCY, are not dissociated, then the two methods of preparation would result in the isolation of isomerides. Whether this suggestion has or has not any foundation in fact it is difficult to say, as very little is yet known as to the influence of the solvent and of the different radicles, and nothing at all as to the influence of configuration on the stability of the quaternary salt; the interesting fact that two such isomerides of different configurations may differ greatly in stability seems to have just been established by Wedekind's most recent work.

Is it not possible, moreover, that stereochemical isomerides of this type might be so similar in outward properties as to be indistinguishable?

Considering these possibilities, it seems premature to accept any view as conclusive until more is known regarding the configuration of nitrogen and of other quinquivalent elements; even with respect to trivalent nitrogen, the experimental evidence is most conflicting. On the one hand, the existence of isomeric oximes, &c., leads to the conclusion that the three nitrogen valencies are *not* situated symmetrically in one plane; on the other, no case is known of the existence of isomeric compounds of the type  $\text{NR}_1\text{R}_2\text{R}_3$ , which is a probable, if not even a necessary, consequence of Hantzsch and Werner's hypothesis.

Mr. G. Tattersall, B.Sc., has taken an active part in this work (p. 918), and Mr. A. Hunter has rendered very able assistance, for which the author desires to express his thanks.

The author is also indebted to the Government Grant Committee of the Royal Society for a grant in aid of these investigations.

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XCH.—*Nitrocamphor and its Derivatives. V. sesqui-Camphorylhydroxylamine, a Product of the Spontaneous Decomposition of Nitrocamphor. VI. Camphoryloxime-anhydride. VII.  $\beta$ -Bromo- $\alpha'$ -nitrocamphor.  $\beta$ - and  $\pi$ -Bromocamphorilyloximes.\**

By T. MARTIN LOWRY, D.Sc.

V. *sesqui*CAMPHORYLHYDROXYLAMINE.

IN the year 1898, a quantity of nitrocamphor was prepared by reducing  $\alpha$ -bromo- $\alpha'$ -nitrocamphor with an alcoholic solution of potassium hydroxide in the manner described in a previous paper (Trans., 1898, 73, 995). On acidifying the alkaline solution, the nitrocamphor separated as an oil which slowly deposited crystals; these were washed with water and alcohol, once recrystallised from alcohol, and stored in a stoppered bottle. A few months ago, Dr. Lapworth drew my attention to the fact that a small sample which I had sent him from this bottle no longer possessed the properties of nitrocamphor, but had in some way undergone a change. As a considerable quantity of material was available and a number of interesting changes had already been investigated (Trans., 1898, 73, 986, 991, and 999; 1899, 75, 211), it appeared desirable to ascertain what products might be formed from this new and unexpected decomposition. Before describing the results of the investigation, it may, however, be pointed out that, like so many other changes, the "spontaneous" decomposition of nitrocamphor is dependent on the presence of impurities. The main stock of material, which was found to have undergone change, was sufficiently purified for all ordinary purposes, but possessed a slight yellow colour and a sweet odour, similar to that of the oil from which it had separated. By crystallising again from alcohol and from benzene, hard, well-formed crystals can be obtained which are quite colourless and odourless. A few crystals which had been purified in this way were unchanged at the end of five years.

In order to ascertain the fate of the nitrocamphor, 20 grams of the changed material and 5 grams of sodium hydroxide were shaken with water and purified ether; a portion of the substance dissolved but a considerable amount of a neutral compound was left which was insoluble in alkali and only sparingly soluble in ether. When 175 grams of the material were treated in this way and the ether allowed to evapor-

\* Preliminary notices of the results recorded in the present communication have appeared in the Proceedings, 1903, 19, 129, 156.

ate, 55 grams of the neutral substance were obtained, whilst the alkaline liquors yielded 85 grams of crystalline nitrocamphor and a few grams of a non-crystalline oil similar to the crude nitrocamphor prepared by reducing bromonitrocamphor in the manner already described.

When crystallised twice from alcohol, the decomposition product was obtained as a white, microcrystalline powder which melted at  $256^{\circ}$  to a brown oil; it dissolved in acetone to the extent of 3.22 grams in 100 c.c. of solution at  $13^{\circ}$ ; two independent determinations of the specific rotatory power in this solvent gave  $[\alpha]_D +33^{\circ}$  at  $13^{\circ}$ . Its melting point, which is very high when contrasted with that of other camphor compounds, and its slight solubility, indicated that condensation of two or more molecules of nitrocamphor had taken place, and molecular weight determinations in boiling benzene solution, made at my request by Mr. F. G. Smith, proved the correctness of this view. Owing to the limited solubility of the substance, the largest rise in the boiling point was only  $0.2^{\circ}$ , and exact numbers could not therefore be expected, but the values obtained,  $M=562, 581, 565, 589, 524$ , and  $528$ , mean,  $558$ , showed clearly that the decomposition product had been formed by the condensation of three molecules of nitrocamphor for which  $M=197$ .

The values obtained on combustion suggested that the condensation had been effected by the elimination of two molecules of water from three molecules of nitrocamphor, but nitrogen determinations showed that one of the three atoms of nitrogen had been eliminated (probably by oxidation to camphoric acid), and that the formula of the substance could be deduced from the equation  $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O + 2C_{10}H_{15}O \cdot NO_2 = C_{30}H_{42}O_8N_2 + H_2O$ . The analytical data were as follows:

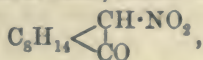
- I. 0.2171 gave 0.5129  $CO_2$  and 0.1470  $H_2O$ . C = 64.43; H = 7.47.
- II. 0.2336 „ 0.5537  $CO_2$  „ 0.1573  $H_2O$ . C = 64.65; H = 7.40.
- III. 0.1514 „ 0.3585  $CO_2$  „ 0.0995  $H_2O$ . C = 64.56; H = 7.35.  
 $C_{30}H_{41}O_7N_3$  requires C = 64.53; H = 7.31 per cent.  
 $C_{20}H_{42}O_8N_2$  „ C = 64.47; H = 7.58 „
- IV. 0.3413 gave 16.0 c.c. moist nitrogen at  $15^{\circ}$  and 746 mm. N = 5.28.
- V. 0.4871 „ 22.2 c.c. „ „  $11^{\circ}$  „ 759 mm. N = 5.43.  
 $C_{30}H_{42}O_8N_2$  requires 5.02 per cent.

To ascertain whether the camphor nucleus had undergone change in any way, experiments were made on the oxidation of the decomposition product. In the first experiment, oxidation was effected by means of concentrated nitric acid (sp. gr. 1.42) diluted with about half its bulk of water. In spite of its high melting point, the substance

readily liquefied in the boiling acid and frothed up into a mass of minute bubbles, a colourless gas being liberated, although not in large quantities. The oxidation product remained liquid until quite cool, but solidified when washed with water and was recrystallised from acetic acid and from alcohol. It had a lower melting point ( $235^{\circ}$ ), a lower specific rotatory power ( $+22^{\circ}$ ), and a greater solubility in acetone than the original material, and when recovered from the solution in acetone was burnt under the impression that a definite oxidation had occurred; the analysis, the third of those given above, agreed exceptionally well with those of the original substance, and it was then found that the final crystallisation from acetone had produced an altogether remarkable effect in freeing the substance from the impurities with which it was mixed, and had raised the melting point through  $20^{\circ}$  to that of the pure substance. This result is perhaps due to the "formation of a compound of camphoric acid with acetone" (Pope, Trans., 1896, 69, 1696) and proved of great service when the synthesis of the substance was attempted. Oxidation with concentrated nitric acid (sp. gr. 1.42) at  $100^{\circ}$  gave the desired result, and the well-crystallised camphoric acid which separated from the acid solution was identified by its appearance and melting point and also by conversion into the anhydride melting at  $215^{\circ}$ .

The formula deduced for the decomposition product may be obtained by subtracting one molecule of hydroxylamine from three molecules of nitrocamphor,  $3C_{10}H_{15}NO_3 = C_{30}H_{42}N_2O_8 + NH_3O$ , and it was therefore thought possible that this base might be present in the changed material. Tests by means of alkaline copper and Nessler solutions gave no indication of the presence of either hydroxylamine or ammonia, and it is therefore possible that the elimination of a nitrogen atom depends on a direct atmospheric oxidation in which elementary nitrogen is produced, and not on a process of hydrolysis.

More important is the fact that the substance has the empirical composition of a camphoric ester of nitrocamphor, for the oxidation experiments show that no profound decomposition has taken place, and the only formulæ that are reasonably possible are those which would represent it as the camphoric ester, either of nitrocamphor,



or of *pseudonitrocamphor*,  $C_8H_{14} \begin{array}{c} \diagup C \cdot NO \cdot OH^* \\ \diagdown CO \end{array}$ , or of the isomeric cam-

\* The formula here employed may be conveniently used to express in a non-controversial manner the three formulæ that have been proposed for the *pseudo*-nitro-compounds, namely,  $>C:N \cdot O \cdot OH$ ,  $>C:N \begin{array}{c} O \\ \parallel \\ OH \end{array}$ , and  $>C \begin{array}{c} N \cdot OH \\ \diagdown O \end{array}$ .



phoryloxime,  $C_8H_{14} \begin{smallmatrix} \text{C:NOH} \\ \text{CO} \end{smallmatrix} O$ .\* Of these, the first is very improbable, for derivatives of normal nitrocamphor have only been prepared either by the action of halogens or by indirect methods, and there is no reason to suppose that in this case esterification would lead to the formation of the so-called "carbon ether."

The second formula, although more worthy of consideration, cannot be reconciled with the low rotatory power of the substance, or with its great stability when heated alone or when boiled with alcoholic potash, as compared with the anhydride of *pseudonitrocamphor*,

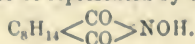
$O \left[ NO : C \begin{smallmatrix} C_8H_{14} \\ CO \end{smallmatrix} \right]_2$ , which very readily yields camphorquinone under

these conditions; the ester is also unchanged when heated with concentrated hydrochloric acid. The third formula is rendered very probable, not only by the process of exclusion, but also because on attempting to prepare acyl derivatives of *pseudonitrocamphor*, either by the action of benzoyl chloride on the potassium salt or by heating the nitro-compound with acetic anhydride and sodium acetate, derivatives of the isomeric camphoryloxime are always produced (Trans., 1898, 73, 999).

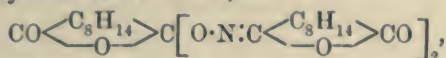
The constitution of the decomposition product having been thus clearly indicated, an attempt was made to prepare it synthetically by heating 1 gram of the oxime and 0.4 gram of camphoric acid at 170° during 2 or 3 hours; a dark product was obtained which was entirely soluble in alkalis, showing that no ester had been formed. In a second attempt, sulphuric acid was employed as a "condensing agent," and the mixture was heated until bubbles of gas were evolved; the product in this case was readily soluble, not only in alkalis, but also in water, and apparently both the acid and the oxime were converted

into sulphocamphoric acid,  $C_8H_{14} \begin{smallmatrix} SO_3H \\ CO_2H \end{smallmatrix}$ , carbon dioxide being eliminated. In a third and successful attempt, made to synthesise the compound by the Schotten-Baumann method from camphoryl chloride and camphoryloxime, the camphoryl chloride from 0.8 gram of camphoric acid was mixed with water and then with 1 gram (= 1 mol. or half the theoretical quantity) of the oxime and enough sodium hydroxide to keep the solution alkaline. A solid soon separated, and the mixture was left for 5 days in order to remove the last traces of camphoryl chloride. The product was then drained, crystallised from spirit and from acetone, and found to be identical with the ester from nitrocamphor.

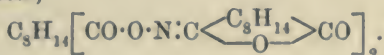
\* Camphoryloxime might also be represented by the symmetrical formula



The substance, which is thus shown to be the camphoric ester of camphoryloxime, is a derivative of hydroxylamine in which the whole of the hydrogen is displaced by camphoryl radicles and is precisely analogous to tribenzoylhydroxylamine,  $\text{NBz}_3\cdot\text{OBz}$ ; it is therefore proposed to call it *sesquicamphorylhydroxylamine*. The exact formula of the substance is, however, involved in the old controversy as to whether the derivatives of dibasic acids should be represented by symmetrical or by unsymmetrical formulæ, and it would be possible to adopt either the wholly symmetrical formula,  $\text{C}_8\text{H}_{14}\left[\text{CO}\cdot\text{O}\cdot\text{N}\left\langle\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right\rangle\text{C}_8\text{H}_{14}\right]_2$ , or the wholly unsymmetrical formula,

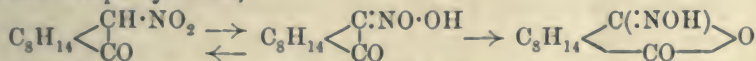


but as the esters of dibasic acids appear to be usually of the symmetrical type, and camphoryloxime is best represented by an unsymmetrical formula, a preference should perhaps be given to the mixed formula for the ester,

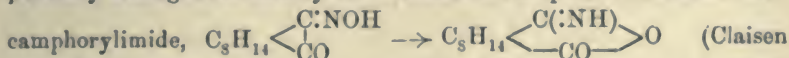


## VI. CAMPHORYLOXIME-ANHYDRIDE.

When nitrocamphor is boiled with concentrated hydrochloric acid, the greater part passes into solution and is converted into the isomeric camphoryloxime,



(*Trans.*, 1898, 73, 999), by an isomeric change of the Beckmann type precisely analogous to that by which *isonitrosocamphor* is converted into



and Manasse, *Annalen*, 1893, 274, 73). But as Cazeneuve pointed out in the paper in which the isomeric change was first described (*Bull. Soc. chim.*, 1889, [iii], 1, 417), nearly 10 per cent. of the substance used is converted into a resinous product which is insoluble in water. When preparing the oxime from nitrocamphor with a view to establishing its constitution (*loc. cit.*), a considerable quantity of the insoluble material was accumulated, and this was recently examined in order to ascertain whether it might not be identical with the *sesquicamphorylhydroxylamine* described above.

The crude material dissolved readily in alcohol, and, on cooling, the solution deposited crystals of a sparingly soluble substance, which, when crystallised three times from alcohol, softened at  $215^\circ$  and melted at  $220^\circ$ . Its specific rotatory power was found to be  $[\alpha]_D + 26.4^\circ$  at

15° in a solution in acetone containing 2.9 grams in 100 c.c. Analysis showed that this substance had the composition of an anhydride of nitrocamphor:

\*0.1630 gave 0.3787 CO<sub>2</sub> and 0.1065 H<sub>2</sub>O. C = 63.36; H = 7.31.

C<sub>20</sub>H<sub>28</sub>O<sub>5</sub>N<sub>2</sub> requires C = 63.79; H = 7.50 per cent.

A nitrogen determination with the once crystallised substance gave a value slightly below the theoretical (found 6.9, calculated 7.46 per cent.). As normal nitrocamphor contains no hydroxyl group and the anhydride of *pseudonitrocamphor* has already been described (*loc. cit.*, p. 996), the compound of which the formation is now recorded must be regarded as the previously unknown anhydride of the camphoryloxime which forms the main product of the action. If the unsymmetrical formula be adopted for the oxime, the anhydride must be written  $\text{CO} \langle \text{C}_8\text{H}_{14} \rangle \text{C}:\text{N} \cdot \text{O} \cdot \text{N}:\text{C} \langle \text{C}_8\text{H}_{14} \rangle \text{CO}$ . This formula is fully in accordance with the properties of the substance, which differs from the isomeric anhydride of *pseudonitrocamphor* in that it yields no trace of camphorquinone either when heated alone or when warmed with alcoholic potash, and does not possess the high dextrorotatory power which characterises the derivatives of *pseudonitrocamphor*.

The formation of an anhydride from camphoryloxime takes place much less readily than in the case of nitrocamphor or *isonitroso*-camphor (Forster, this vol., p. 530), and it appeared possible that this anhydride had been formed by isomeric change from the anhydride of *pseudonitrocamphor*, a compound which might conceivably be produced in the initial stages. This isomeric change was, however, found not to take place under the conditions of the action, and the production of the anhydride cannot therefore be explained in this way. Neither can it have been formed by the dehydration of the oxime, for the amount of resin produced is not increased by prolonged heating of the strongly acid solution, and, moreover, no resin whatever is produced when the pure oxime is heated with concentrated hydrochloric acid. The production of the anhydride must therefore be ascribed to the condensation of some intermediate product of change, such, for instance, as the little understood hydrochloride described by Cazeneuve (*ibid.*, p. 243), unless, perchance, the violence of the action in its initial stages is capable of bringing about a condensation of camphoryloxime which does not take place under more usual conditions.

The analogy between camphoryloxime,  $\text{C}_8\text{H}_{14} \langle \text{C}(\text{NOH}) \rangle \text{O}$ , and

\* This analysis was carried out with the help of the potash absorption apparatus recently described by Wetzel (*Ber.*, 1903, **36**, 162); the analysis was made exceedingly rapidly, and the combustion, in both air and oxygen, was completed within 25 minutes, a further time being allowed for displacing the oxygen by air.



isonitrosocamphor,  $C_8H_{14} \begin{smallmatrix} \text{C:NOH} \\ \text{CO} \end{smallmatrix}$ , is perhaps more apparent than

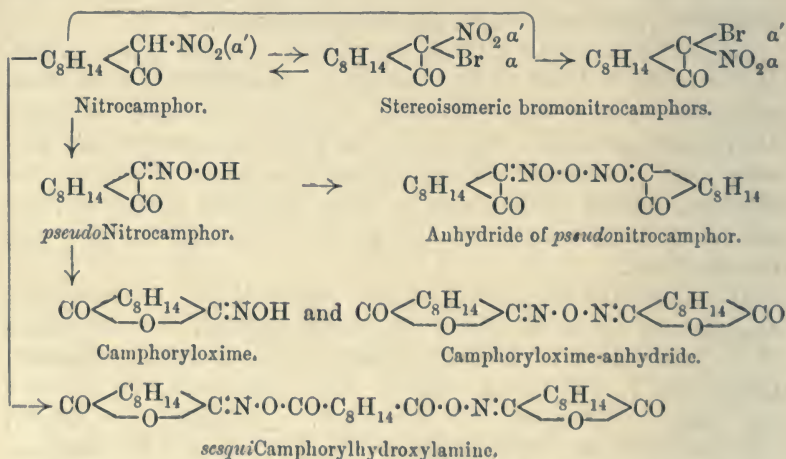
real, for the introduction or removal of the acidic oxygen atom entirely alters the chemical properties of the substance. It appeared, however, to be desirable to ascertain whether some of the many methods used by Forster for preparing the anhydride of isonitrosocamphor could be successfully applied to camphoryloxime. The method recommended by Forster as being the best for the purpose consists in boiling the benzoyl derivative and the potassium salt of the oxime together in a neutral solvent such as benzene; accordingly 5 grams of benzoylcamphorylhydroxylamine were dissolved in benzene and boiled during 12 hours with a slight excess of the potassium salt of camphoryloxime; on filtering the solution, the benzoyl derivative was recovered unchanged and no formation of anhydride had taken place. An attempt was also made to prepare the anhydride by shaking an aqueous solution of the sodium salt with a mixture of ether and acetic anhydride, but this also gave a negative result, the oxime being converted quantitatively into the acetyl derivative.

Another unsuccessful attempt was made to prepare the anhydride by the action of 1 mol. of phosphorus pentachloride on 2 mols. of the potassium salt of the oxime, as in the preparation of acetic anhydride; interaction took place, and the mixture became very viscid, but on diluting with water nearly the whole of the material dissolved, leaving behind only a small, flocculent precipitate, the amount of which was insufficient to allow of its being identified with the anhydride.

The successful preparation of the anhydride of the oxime was accomplished by an altogether unexpected method. In the course of the investigation of the constitution of camphoryloxime ("campho-nitrophenol"), which has already been mentioned, an attempt was made to brominate the compound. The oxime (10 grams) was dissolved in an excess of potassium carbonate and bromine was added until it gave a permanent coloration; a white compound was precipitated which separated from alcohol in a viscous condition and was therefore redissolved and poured into water. Shortly afterwards, a clue was obtained as to the real nature of the oxime and the bromination product was put aside, and was not further examined until quite recently. It was then found that the crude material contained very little bromine, and separated as a crystalline deposit on allowing an alcoholic solution to evaporate. The separated solid was recrystallised three times from alcohol and was found to be identical with the anhydride obtained as a bye-product in the preparation of the oxime. The substance prepared by bromination melted in exactly the same manner as the latter, sintering over about  $5^\circ$  and melting indefinitely

with partial decomposition to a light brown liquid; when the two specimens were heated together, the bromination product melted about  $3^\circ$  higher than the other, but the specific rotatory powers of the two preparations agreed exceedingly closely, the bromination product giving  $[\alpha]_D + 26.7^\circ$  at  $14^\circ$  in a solution in acetone containing 2 grams in 100 c.c., whilst the value given above for the bye-product from the preparation of the oxime is  $[\alpha]_D + 26.4^\circ$ .

The compound now described is of interest as affording yet another illustration of the extraordinary fertility of nitrocamphor in yielding new substances, often of unknown types, and undergoing changes for which no precedents are available. The most important of these changes are summarised in the scheme given below, but it may be added that the anhydride only forms about 10 per cent. of the resinous bye-product, or 1 per cent. of the weight of nitrocamphor used, and it is at least possible that the remaining 9 per cent. which is unaccounted for, may be found to yield other new derivatives.



## VII. $\beta$ -BROMO- $\alpha'$ -NITROCAMPHOR, $\beta$ - AND $\pi$ -BROMOCAMPHORYLOXIMES.

The results which have followed from the investigation of nitrocamphor, and especially the discovery of the method of studying dynamic isomerism by means of the mutarotation of freshly prepared solutions, have lent a great interest to all those optically active substances in which similar phenomena are likely to be observed. The method, introduced for the first time in the case of nitrocamphor, is easier to carry out, and is of wider applicability than any of the methods which are available for the study of optically inactive com-

pounds, and by its help it is possible to detect with certainty cases of isomeric change in which the velocity of change is so great that equilibrium is reached within a few minutes, or in which the extent of the change is so small that the presence of an isomeride could scarcely be detected by any other method. The camphor nucleus lends itself in a remarkable way to the production of substances representing nearly every type of dynamic isomerism, and with its help the method has already been successfully applied, not only to the study of the isomerism of the nitro-compounds, but also to that of the hydrazones and azo-compounds (Lapworth and Hann, *Trans.*, 1902, 81, 1508), the diketones (Forster, *Trans.*, 1901, 79, 987), and the oximes (Forster, *this vol.*, p. 514), whilst Lapworth and Hann (*Trans.*, 1902, 81, 1491, 1499) have recently investigated the optically active analogues of ethyl acetoacetate and ethyl formylphenylacetate.

The isomerism of the nitro-derivatives of camphor has already been somewhat fully studied, but in view of the great advance which resulted from the extension of the investigation of nitrocamphor to that of its  $\pi$ -bromo-derivative, and the still greater differences which were observed between nitrocamphor,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NO}_2 \\ \text{CO} \end{smallmatrix}$ , and nitrocamphane,

$C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \text{CH} \cdot \text{NO}_2 \end{smallmatrix}$  (Forster, *Trans.*, 1900, 77, 251)—compounds which scarcely differ except in the replacement of the CO by the  $\text{CH}_2$  group, and yet are altogether different in chemical behaviour and in the character of the equilibrium between the normal and pseudo-forms—it appeared to be very desirable to continue the investigation, and to prepare, if possible, the  $\beta$ -bromo-derivative of nitrocamphor.

$\alpha\beta$ -Dibromo- $\alpha'$ -nitrocamphor,  $C_8H_{13}\text{Br} \begin{smallmatrix} \text{CBr} \cdot \text{NO}_2 \\ \text{CO} \end{smallmatrix}$ , was prepared many years ago by Kachler and Spitzer (*Monatsh.*, 1882, 3, 218; 1883, 4, 566) by boiling  $\alpha\beta$ -dibromocamphor,  $C_8H_{13}\text{Br} \begin{smallmatrix} \text{CHBr} \\ \text{CO} \end{smallmatrix}$ , with concentrated nitric acid, but for more than twenty years nothing further was done with the  $\beta$ -derivatives of camphor until new methods of preparation led to the discovery of the parent substance,  $C_8H_{13}\text{Br} \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix}$  (Armstrong and Lowry, *Trans.*, 1902, 81, 1464; Forster, *ibid.*, p. 264), and to the determination of its constitution. Unlike the  $\pi$ -bromo-compounds, the  $\beta$ -bromo-derivatives of camphor are very sensitive to the action of hydrolysing and reducing agents, so much so that the whole of the  $\beta$ -bromine can be eliminated by the action of alcoholic potash (Kachler and Spitzer, *loc. cit.*; Forster, *loc. cit.*, p. 270), and a considerable proportion is liberated when the substances are



oxidised with nitric acid (Armstrong and Lowry, *loc. cit.*, p. 1467). In attempting to reduce the dibromonitro-compound, it was therefore necessary to proceed very cautiously, and it was a matter of satisfaction when it was found that, by using the theoretical quantity of alcoholic potash or sodium ethoxide, the reduction could be readily effected, and gave a solid product as in the case of the isomeric  $\pi$ -bromonitrocamphor.

As might perhaps have been anticipated,  $\beta$ -bromonitrocamphor differs widely from nitrocamphor, but closely resembles the  $\pi$ -bromo-derivative. Thus the pseudo, not the normal, form separates from solution on slow crystallisation, whereas mixtures of the two forms are produced by rapid crystallisation; it has not been found possible, as yet, to isolate the normal form either by rapid evaporation of the solution and mechanical separation of the crystals, as in the case of  $\pi$ -bromonitrocamphor, or by making use of hydroxylic solvents, as in the case of the oximes described by Dr. Whiteley (this vol., p. 34). Again, the 'equilibrium temperature' (Trans., 1899, 75, 233) at which the solid pseudo-form is in stable equilibrium with the liquid mixture can be readily observed, as in the case of the  $\pi$ -bromo-compound, by fusing the substance, allowing it to crystallise by cooling, and noting the temperature at which the solid melts when again heated; nitrocamphor, as has already been pointed out (*loc. cit.*, p. 233), does not crystallise when cooled after fusion. Other points of resemblance will be noted later, and it is quite possible that the interesting results which have accrued from the study of  $\beta$ -bromonitrocamphor might have followed with equal readiness from  $\pi$ -bromonitrocamphor if there had been the same motive for resuming the study of this substance as there was for investigating its unknown  $\beta$ -isomeride.

The remarkable isomeric change which nitrocamphor undergoes when heated with concentrated hydrochloric acid (Cazeneuve, *Bull. Soc. chim.*, 1889, [iii], 1, 417) and when benzoylated or acetylated (Trans., 1898, 73, 999) has already been shown to be a normal Beckmann change, the product being identified as an oxime of camphoric anhydride. A similar change has been observed by Lapworth and Kipping (Trans., 1896, 69, 318) in the case of  $\pi$ -bromonitrocamphor, although at the time the nature of the change was not understood; as the necessary material was available, and it was desirable to prepare the acetate and benzoate of Lapworth's compound for comparison with the isomeric  $\beta$ -compounds, the oxime of  $\pi$ -bromocamphoric anhydride was prepared synthetically, as well as from  $\pi$ -bromonitrocamphor, and its constitution was further established by hydrolysing it to hydroxylamine and  $\pi$ -bromocamphoric acid.  $\beta$ -Bromonitrocamphor undergoes a similar isomeric change, although

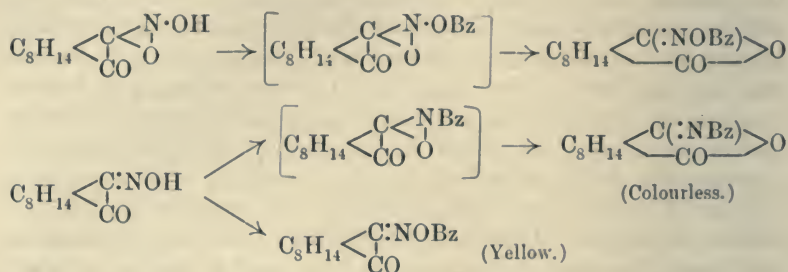
less readily than nitrocamphor; this difference might be explained as being due to the higher melting point of the substance, but it is more likely that the bromine atom has a definite action in retarding the isomeric change. This view receives support from the fact that whilst nitrocamphor can be acetylated or benzoylated without difficulty, yielding the acetyl or benzoyl derivative of camphoryloxime, Lapworth and Kipping have shown (*ibid.*, p. 314) that  $\pi$ -bromopseudonitrocamphor can be boiled with acetyl chloride or acetic anhydride without undergoing change, and it has also been found that  $\beta$ -bromopseudonitrocamphor yields no trace of a benzoyl derivative when an aqueous solution of its potassium salt is shaken with benzoyl chloride. A further illustration of the inhibiting effect of the bromine atom on the general reactivity of the compound is afforded by the impossibility of preparing an anhydride from  $\beta$ - or  $\pi$ -bromonitrocamphor, although nitrocamphor and isonitrosocamphor readily yield such compounds.

Mention must also be made of the important influence exercised by the ketonic group in this series of compounds. This will be brought out most clearly if a comparison be made between nitrocamphor and its bromo-derivatives on the one hand, and nitrocamphane on the other. The effect on the equilibrium between the normal and pseudo-forms is very striking, for whereas in the absence of a keto-group, pseudonitrocamphane is a labile compound and passes completely into the normal form in the course of a few hours, normal nitrocamphor undergoes in solution a partial isomeric change in the reverse direction, and in the  $\beta$ - and  $\pi$ -bromo-derivatives the effect of the keto-group is so far reinforced by the bromine atom that the pseudo-form is actually the one that is stable in contact with the solution. The keto-group also appears to be directly concerned in the isomeric change to camphoryloxime, for in the absence of this group the potassium salt of pseudonitrocamphane can be completely benzoylated without passing into the oxime. The suggestion (Trans., 1898, 73, 1000) that in this case the pseudo, not the normal, form is that which undergoes change, receives support from the fact that normal nitrocamphane, which has no tendency to pass into the pseudo-form, can be dissolved in concentrated sulphuric acid, and reprecipitated unchanged by diluting with water.

The work on nitrocamphor and its derivatives acquires additional interest from the many opportunities that occur of comparing and contrasting their behaviour with that of the analogous isonitroso-compounds which are being investigated by Forster. The chief results of the comparison may be briefly stated as follows: (1) The production of two benzoyl derivatives from isonitrosocamphor places it in an intermediate position between pseudonitrocamphor, which undergoes complete isomeric change, and pseudonitrocamphane, which is



unchanged when benzoylated; the resemblance is most obvious if the formation of Forster's colourless benzoate is regarded as a sequel to the benzoylation of the *isooxime* thus:



(2) The comparison also raises the question as to the formulæ to be assigned to the *pseudonitro*-compounds, for if these be written as  $>\text{C}:\text{N} \begin{array}{c} \text{O} \\ \diagdown \\ \text{OH} \end{array}$  the *isooximes* ought also to be formulated as  $>\text{C}:\text{NH}:\text{O}$ ,

but if the *isooximes* be represented in the usual way,  $>\text{C} \begin{array}{c} \diagup \text{NH} \diagdown \\ \text{O} \end{array}$ , then the *pseudonitro*-compounds should also be indicated by  $>\text{C} \begin{array}{c} \diagup \text{N}\cdot\text{OH} \diagdown \\ \text{O} \end{array}$ .

(3) The question is also raised as to whether it is the normal or the pseudo-form of the oxime that undergoes the Beckmann isomeric change; the view usually taken is that the normal form is that which is directly concerned, but the alternative view is at least entitled to careful consideration. (4) Finally, it will be of interest to know whether the analogy can be extended to the mutarotatory form of *isonitroso*-camphor (Forster, this vol., 518) by regarding the two modifications as the normal and pseudo-forms of the oxime rather than as stereo-isomerides.

*β-Bromonitrocampor*.—Five grams of well-crystallised dibromonitrocampor were dissolved in 50 grams of absolute alcohol and the theoretical quantity of potassium hydroxide was added in concentrated aqueous solution; the mixture was boiled during 2 or 3 minutes until potassium bromide separated, and was then poured into water. On the next day, a small amount of solid, afterwards found to be tri-bromocampor, had separated, and, after extracting the alkaline solution with ether in order to remove a small amount of oily impurity, the nitro-compound was precipitated by hydrochloric acid, left for a day to separate completely, and then drained and crystallised from spirit. In the later experiments, the reduction was effected in absolute alcoholic solution by means of the calculated quantity of sodium ethoxide, but even when all possible precautions were taken a considerable loss of



material occurred; the yield of *crystalline* dibromonitrocamphor obtained after brominating  $\beta$ -bromocamphor, boiling with nitric acid, and crystallising the product of nitration from acetic acid is about 45 per cent. of the weight of bromocamphor used, and the yield of bromonitrocamphor is about one-third of the weight of dibromonitrocamphor employed in the reduction.  $\beta$ -Bromonitrocamphor, prepared in this way, was obtained as a crystalline powder, which was found to consist of a mixture of the normal and pseudo-forms,  $C_8H_{13}Br$   $\begin{array}{c} \text{CH}\cdot\text{NO}_2 \\ | \\ \text{CO} \end{array}$

and  $C_8H_{13}Br$   $\begin{array}{c} \text{C}\cdot\text{NO}\cdot\text{OH} \\ | \\ \text{CO} \end{array}$ ; it softened at  $100^\circ$  and melted indefinitely at about  $114^\circ$ , but when allowed to crystallise after fusion it remelted sharply at  $100^\circ$ ; this is, therefore, the 'equilibrium temperature' at which the solid pseudo-form is in stable equilibrium with the liquid mixture; the crystalline powder obtained by rapid crystallisation contained a slightly larger proportion of the pseudo-form than that which is normally present in the solution, and freshly-prepared solutions exhibited mutarotation.

0.2326 gave 0.1617 AgBr. Br = 29.6 (calc. 29.0 per cent.).

The *pseudo*-form was obtained in a pure state by slow evaporation of a solution of the nitro-compound in benzene or ethyl acetate; it melted at  $132^\circ$ , but decomposed slightly at this temperature, and remelted at or below  $96^\circ$ , according to the length of time during which it had been heated; the extent to which the decomposition had proceeded could be gauged by the increase in the intensity of the yellow colour of the material, which probably decomposes into  $\beta$ -bromocamphorquinone. Attempts were made to isolate the *normal* form by crystallising from hydroxylic solvents, but these were not successful, for a solution in methyl alcohol yielded a mixture of the two forms on slow evaporation, and a solution in formic acid apparently gave rise to the isomeric oxime, for on diluting with water, after an interval of two or three weeks during which no crystallisation had taken place, the greater part of the material remained in solution, and the small amount which separated was entirely different in its properties from the original bromonitrocamphor. A solution in acetic acid gave the pure pseudo-form on slow crystallisation.

The *potassium* salt,  $C_{10}H_{14}NO_3K, 2H_2O$ , of the pseudo-form separated from water in glistening needles. The specific rotatory power of an aqueous solution containing 0.7043 gram of the dry potassium salt in 15 c.c. of solution was found to be  $[\alpha]_D + 91^\circ$  at  $12^\circ$ ; or if the specific rotatory power be reckoned on the  $\beta$ -bromonitrocamphor contained in the salt, the value for the *pseudonitro*-compound in this form would be  $[\alpha]_D + 103^\circ$ .

0.8010 lost 0.0791 moisture.

$H_2O = 11.0$  (on dry salt); calculated, 11.42 per cent.

An attempt to prepare the benzoate of  $\beta$ -bromopseudonitrocamphor by the Schotten-Baumann method gave only a negative result; the benzoyl chloride passed gradually into the solution, leaving no trace of an insoluble benzoyl derivative. Similarly, it was not found possible to prepare an anhydride of the pseudo-form by heating above the melting point. In both these respects,  $\beta$ -bromonitrocamphor differs from nitrocamphor, but behaves in the same way as the isomeric  $\pi$ -bromo-compound.

$\beta$ -Bromocamphoroxime,  $C_8H_{13}Br \left\langle \begin{array}{c} C(:NOH) \\ \text{CO} \end{array} \right\rangle O$ , was prepared by heating  $\beta$ -bromonitrocamphor with concentrated hydrochloric acid in a water-bath during half an hour; nearly the whole of the substance passed into solution and was separated by filtration from a little resin which was formed as a bye-product (compare p. 957); on diluting the filtrate with water, the oxime, which is readily soluble in strong hydrochloric acid, but very sparingly so in water, was precipitated in minute needles which were drained and washed with a little cold water. Like camphoroxime and the  $\pi$ -bromo-compound,  $\beta$ -bromocamphoroxime crystallises from water with  $1H_2O$ :

0.9872 lost 0.0629 moisture.

$H_2O = 6.81$  (on dry substance); calculated, 6.50 per cent.

The hydrate melts at  $111^\circ$  with liberation of steam. The dry substance was dissolved in benzene, in which it is only sparingly soluble even on boiling, and crystallised, on cooling, in bright, glistening needles which melted at  $112^\circ$ ; a solution in chloroform saturated at  $13^\circ$  contained 2.20 grams in 100 c.c. of solution and gave  $[\alpha]_D + 10.2^\circ$ . In order to prepare the *acetyl* derivative, the oxime was boiled with acetic anhydride, and the solution diluted with alcohol and then with water; the acetate separated as an oil, but crystallised when stirred: the substance was then redissolved in the same liquor, filtered, allowed to crystallise, and then recrystallised from slightly dilute alcohol, from which it separated in very light, minute flakes, which melted at  $112^\circ$ , did not recrystallise when cooled after fusion, and gave  $[\alpha]_D + 3^\circ$  at  $15^\circ$  in a solution in acetone containing 2.36 grams in 100 c.c.

0.1746 gave 0.1030 AgBr. Br = 25.21.

$C_{12}H_{16}O_4NBr$  requires 25.16 per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann method, is only moderately soluble in hot alcohol, and crystallises in needles as the solution cools; it melts at  $134^\circ$  and gave  $[\alpha]_D + 11^\circ$  at  $12^\circ$  in a solution in acetone containing 1.57 grams in 100 c.c.

0.2096 gave 0.1041 AgBr. Br = 21.12.

$C_{17}H_{15}O_4NBr$  requires 21.05 per cent.

*$\pi$ -Bromocamphoryloxime.*—In order to establish definitely the constitution of Lapworth's "*iso- $\pi$ -bromonitrocamphor*" (Trans., 1896, 69, 318), the substance was hydrolysed by heating in a sealed tube with concentrated hydrochloric acid; the aqueous solution gave the usual tests for hydroxylamine, but the solid was too much charred to allow of its identification as  $\pi$ -bromocamphoric acid. As, however, a quantity of  $\pi$ -bromocamphoric acid had been obtained as a bye-product in the preparation of  $\pi$ -bromonitrocamphor, and it was desired to prepare the acetyl and benzoyl derivatives of the oxime for comparison with those of the  $\beta$ -bromo-oxime, the acid was converted into its anhydride and treated with hydroxylamine in the manner previously employed in the synthesis of camphoryloxime (Trans., 1898, 73, 1005); the synthetical oxime, its hydrate, acetyl and benzoyl derivatives agreed so closely with those of the substance prepared from  $\pi$ -bromonitrocamphor that they do not merit separate description. *Acetyl- $\pi$ -bromocamphoryloxime*,  $C_8H_{13}Br \left\langle \begin{smallmatrix} N:NOAc \\ CO \end{smallmatrix} \right\rangle O$ , was prepared by Lap-

worth by boiling the oxime with acetic anhydride, but its physical constants were not given; it is only sparingly soluble in alcohol, and separates, like the  $\beta$ -isomeride, in minute, glistening scales; it melts at  $171^\circ$  (the  $\beta$ -isomeride melts at  $112^\circ$ ) and gave  $[\alpha]_D +1.3^\circ$  at  $13^\circ$  in a solution in acetone containing 51.4 grams per 100 c.c.

The *benzoyl* derivative, which is much less soluble, about 50 c.c. of boiling alcohol being required to dissolve a gram, crystallises in flat needles united in feathery aggregates and melts at  $185^\circ$ . In a solution in acetone containing 3.4 grams per 100 c.c. it gave  $[\alpha]_D +46.3^\circ$  at  $13^\circ$ .

As the three series of compounds are now complete, a table is given showing the melting points of the more important derivatives of nitrocamphor and camphoric acid.



| Parent substance.   | Unsubstituted. |                  | $\pi$ -Bromo-derivative. |                   | $\beta$ -Bromo-derivative. |                   |
|---|----------------|------------------|--------------------------|-------------------|----------------------------|-------------------|
|   | M. p.          | $[\alpha]_D$     | M. p.                    | $[\alpha]_D$      | M. p.                      | $[\alpha]_D$      |
| Camphoric acid, $C_8H_{14}<\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}>$ ..... | 187°           | +47° (alcohol)   | 216—217°                 | +41° (alcohol)    | 210°                       | +39° (alcohol)    |
| Camphoric anhydride, $C_8H_{14}<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>O$ ..... | 216            | -1° (chloroform) | 155—156                  | -37° (acetone)    | 142                        | -3° (acetone)     |
| Camphoryloxime, $C_8H_{14}<\begin{smallmatrix} C(:NOH) \\ CO \end{smallmatrix}>O$ ...   | 223            | +7° (chloroform) | 137—138                  | +53° (chloroform) | 112                        | +10° (chloroform) |
| “ hydrate .....   | 70             | —                | 109—112                  | —                 | 111                        | —                 |
| “ acetyl derivative .....   | 115            | +7° (chloroform) | 171                      | +41° (acetone)    | 112                        | +3° (acetone)     |
| “ benzoyl derivative .....  | 138            | +9° (chloroform) | 185                      | +46° (acetone)    | 134                        | +11° (acetone)    |
| Nitrocamphor :  |                |                  |                          |                   |                            |                   |
| Normal .....  | 102            | 124° (benzene)   | 108                      | -51° (benzene)    | —                          | —                 |
| Pseudo .....  | —              | —                | 142                      | +188° (benzene)   | 132                        | 0° (benzene)      |
| Equilibrium mixture .....   | —              | -104° (benzene)  | 126                      | -38° (benzene)    | 100                        | -80° (benzene)    |

XCIII.—*The Estimation of Arsenic in Fuel.*

By T. E. THORPE, C.B., F.R.S.

THE inquiry which followed the lamentable outbreak of poisoning in Lancashire, due to the accidental occurrence of arsenic in beer, has shown that articles of food or drink may become contaminated with arsenic by reason of the presence of that element in fuel. It has been proved, for example, that malt may become admixed with arsenic owing to arsenical pyrites, and possibly other combinations of arsenic, being contained in the fuel which may have been used in preparing it, and maltsters are now under the necessity of exercising care in the selection of the coal or coke to be employed in kilning.

In this communication is given an account of a method of determining the amount of arsenic in fuels which has been worked out in conformity with the recommendation of the Royal Commission on Arsenical Poisoning that the Board of Inland Revenue should prescribe for the different materials used in the preparation of the individual ingredients of beer an adequate test by which their freedom from arsenic may be ascertained. This method is fairly rapid in execution, is accurate, and it has the further merit of directly distinguishing between the arsenic which is volatilised on burning the fuel and that which remains fixed in the ash. The process consists simply in burning a known quantity of the finely-powdered coal or coke in a stream of oxygen, passing the products of combustion through a suitable absorbing apparatus, and determining the amount of arsenic so absorbed as well as that left in the ash.

A piece of hard glass tube, *A*, about 60 cm. long, is drawn out and the drawn-out portion bent, as seen in Fig. 1 (p. 970).

Ten grams of the finely-powdered sample of fuel are then introduced into the tube in such manner that it occupies about 30 cm. of the length of the tube, leaving empty about 6 cm. of the tube next to the bent and drawn-out portion. A convenient method of introducing the fuel is to distribute it along a stout glazed cardboard trough or gutter which can readily be inserted in the tube held in a horizontal position and with the bent portion pointing vertically upwards. On turning the tube round through  $180^\circ$ , so that the bent portion points downwards, the powdered coal falls from the gutter and is loosely distributed along the length of the tube, when the cardboard gutter may be withdrawn. The drawn-out portion of the tube is then connected with the absorption apparatus, *B*, containing dilute sulphuric acid. A convenient form of apparatus consists of a modified de Koninck absorption tube, the straight limb of which contains glass beads or

short lengths of thin glass tubing, so as to offer a considerable wetted surface to the passage of the gaseous products of combustion. The hard glass tube, *A*, is placed in an ordinary combustion furnace and connected with an oxygen reservoir. The burners of the furnace beneath the empty portion of the tube are first lighted, a rapid current of oxygen passing meanwhile through the apparatus. The powdered fuel is then heated at the place where the stream of oxygen first impinges on it. As soon as the combustion has started, very little external heat will be required, and the coal or coke gradually burns away without the formation of soot or tarry products. The whole operation is under perfect control, and is finished in from two to three hours, depending on the nature of the fuel. The ash is left

FIG. 1.—*Apparatus for estimating arsenic in fuel.*

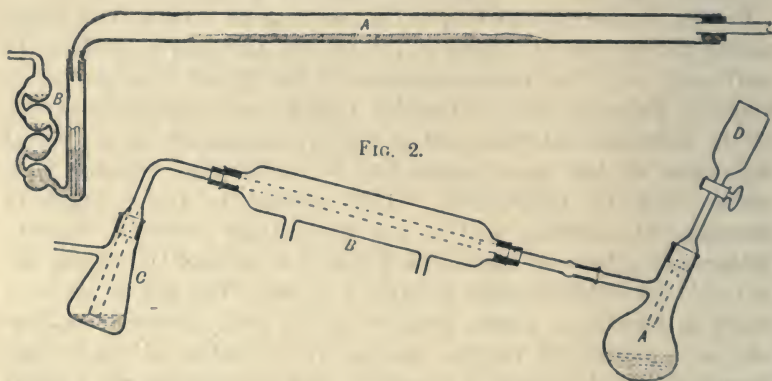


FIG. 1.

*A.*—Hard glass tube.  
*B.*—Absorption tube.

FIG. 2.

*A.*—Distillation flask.  
*B.*—Condenser.  
*C.*—Flask for receiving distillate.  
*D.*—Funnel.

in a loose, pulverulent form, and is readily detached from the tube. The arsenic present in the fuel will be found partly in the ash and partly in the constricted end of the hard glass tube and in the liquid in the absorption apparatus.

To determine the amount of arsenic retained by the ash, this is shaken out into a Würtz flask, *A*, of about 100 c.c. capacity, which is then attached, preferably by means of ground glass joints, as shown in Fig. 2, to a small reflux condenser, *B*, connected with a flask, *C*, of about 70 c.c. capacity, containing about 10 c.c. of arsenic-free hydrochloric acid (sp. gr. 1.1). Into the flask, *A*, containing the coal ash, 25 c.c. of arsenic-free hydrochloric acid, contain-



ing 0.25 c.c. of bromine, are added by means of the ground-in tap-funnel, *D*. In practice, it is convenient to prepare a stock of brominated hydrochloric acid by adding 1 c.c. of bromine to each 100 c.c. of acid (sp. gr. 1.1). The flask is then heated, and the liquid maintained in gentle ebullition for about two hours. After cooling, about a gram of potassium metabisulphite is added, and the liquid again heated until the free bromine disappears. The solution is filtered from the suspended silica, which, together with the small filter, is washed with the acid contained in the small flask, *C*. Unless the silica is removed, the solution is apt to boil irregularly, and it is difficult to distil it properly. The filtered solution is returned to the distilling flask, still connected with the reflux condenser, and boiled to expel the sulphurous acid. The condenser is then reversed and the liquid distilled into the small flask, *C*, the distillation being continued until the residue in the flask, *A*, is syrupy, when a further addition of 10 c.c. of hydrochloric acid is made to the residue and the solution again distilled. The total distillate is made up to 100 c.c. and an aliquot portion taken for testing. This is transferred to a small porcelain dish, 5 c.c. of pure nitric acid (sp. gr. 1.4) and 2 c.c. of pure concentrated sulphuric acid are added, and the solution evaporated until fumes of sulphuric acid are freely evolved. The dish is cooled and the liquid diluted with about 20 c.c. of water and transferred to a small flask. Half a gram of potassium metabisulphite is added and the solution boiled until free from sulphurous acid, and when cold used for the test.

To determine the amount of arsenic which is volatilised in the combustion of the fuel, the acid in the absorption tube is poured into a small beaker and the absorption tube rinsed with a small quantity of water. The end of the hard glass tube is then well washed by repeatedly drawing the liquid in the small beaker into it. Finally, the hard glass tube is rinsed out with a little more acid and the whole of the solution and washings made up to 50 c.c. Of this, 25 c.c. are taken and used directly for the test.

The estimation of the arsenic in the solutions may be made by means of an electrolytic method for detecting and estimating small quantities of arsenic, which has been worked out in this laboratory, and which is the subject of a subsequent communication; or it may be made by means of the Marsh apparatus, but in that case it is unnecessary to remove the hydrochloric acid by evaporation with nitric and sulphuric acids.

In either case, the amount of arsenic obtained is estimated by comparison with arsenic deposits obtained from known quantities of arsenious oxide.

To test the method, a sample of coal, about 4 lbs. in weight, taken

from a Lincolnshire malting, was broken into small pieces; a portion, about 1 lb. in weight, was reduced to a fine powder by grinding in a small so-called Kugelmühle, and known portions of the coal were then treated in the manner described. The results of two experiments, expressed in grains per lb., were as follows:

|                        | Expt. 1. | Expt. 2. |
|------------------------|----------|----------|
| Volatile arsenic ...   | nil      | nil      |
| Fixed arsenic (in ash) | 0.031    | 0.033    |

To prove that fuel containing arsenical pyrites would yield its arsenic when treated in the manner described, known quantities of arsenical pyrites containing a known amount of arsenic were added to the coal and the process repeated. The arsenical pyrites employed contained 43.36 per cent. of arsenic as the mean of two determinations: (1) 43.49, (2) 43.24 per cent.

The details are as follows:

Expt. I. Ten grams of the coal containing 0.00045 per cent. of fixed arsenic (equivalent to 0.032 grain per lb.) were mixed with 0.0188 gram of the arsenical pyrites, the mixture ignited in oxygen in the manner described, and the amounts of volatile and fixed arsenic respectively determined.

(1) *Volatile Arsenic*.—The contents of the absorption apparatus and the washings of the combustion tube were made up to 200 c.c.; 25 c.c. of this solution were further diluted to 200 c.c., and 25 c.c. of this second solution were employed to furnish the arsenic deposit as described. The amount of the deposit was equivalent to 0.012 mgm. of arsenious oxide, equal to 0.768 mgm. of volatilised arsenious oxide.

(2) *Fixed Arsenic*.—The ash was heated with brominated hydrochloric acid, and, after the addition of potassium metabisulphite, was filtered from silica; the solution was returned to the flask, the sulphurous acid expelled by boiling, and the arsenious chloride distilled. The distillate was made up to 150 c.c.; 20 c.c. of this were diluted to one litre, and 15 c.c. of the diluted liquid were used to furnish a deposit, the amount of which was judged to be equivalent to 0.02 mgm. of arsenious oxide, this being equal to 0.010 gram in the entire solution.

To check this estimation, the remaining 130 c.c. of the original solution were treated with sulphuretted hydrogen, and the arsenious sulphide weighed in a Gooch crucible. The amount was equivalent to 0.01058 gram of arsenious oxide in the whole distillate.

The complete results are:

| Arsenious oxide found. |                | Arsenious oxide taken.    |                |
|------------------------|----------------|---------------------------|----------------|
| Volatile .....         | 0·000768       | In 0·0188 gram of pyrites | 0·010791       |
| Fixed .....            | 0·01058        | In 10 grams of coal ...   | 0·000045       |
|                        | <hr/> 0·011348 |                           | <hr/> 0·010836 |

Expt. II.—Carried out precisely as No. I, except that 0·0178 gram of pyrites was used.

The results were:

| Arsenious oxide found. |               | Arsenious oxide taken.    |                |
|------------------------|---------------|---------------------------|----------------|
| Volatile .....         | 0·00094       | In 0·0178 gram of pyrites | 0·010217       |
| Fixed .....            | 0·00983       | In 10 grams of coal ...   | 0·000045       |
|                        | <hr/> 0·01077 |                           | <hr/> 0·010262 |

Expt. III.—Carried out as Nos. I and II, except that 0·0186 gram of pyrites was used.

The results were:

| Arsenious oxide found. |               | Arsenious oxide taken.    |                |
|------------------------|---------------|---------------------------|----------------|
| Volatile .....         | 0·00201       | In 0·0186 gram of pyrites | 0·010676       |
| Fixed .....            | 0·00917       | In 10 grams of coal ...   | 0·000045       |
|                        | <hr/> 0·01118 |                           | <hr/> 0·010721 |

The agreement between the amount of arsenious oxide found and that calculated may be considered satisfactory in the three experiments, and shows that the whole of the arsenic which may be present in the pyrites contained in coal may be obtained or accounted for by the method described.

That by far the greater quantity of the arsenic which may be present in fuel is not volatilised, but is retained by the ash, is confirmed by similar determinations made on a variety of fuels. Thus, it was found that a North Country gas coke yielded no volatile arsenic, but the ash contained arsenic to the extent of 0·28 grain to 1 pound of fuel. An oven coke, also made from a North Country coal, yielded 0·25 grain of fixed arsenic per pound of fuel, but no volatile arsenic.

This would seem to show that the greater portion of the arsenic which may be found on malt has been deposited on it in the form of coal ash, and ought, therefore, to be removed from it by brushing and screening.

NOTE ADDED JULY 6th, 1903.—Since the printing of this communication, Mr. Wood Smith has drawn my attention to the fact that he, in conjunction with Mr. R. L. Jenks, has described a very similar process upwards of 2 years ago (*J. Soc. Chem. Ind.*, 1901, 20, 437). I regret that I had overlooked this prior communication, and I beg



therefore to tender my apologies to the authors for omitting to make reference to it. Combustion of a fuel in oxygen, or as preferred by Messrs. Wood Smith and Jenks, in air, can hardly, however, be regarded as novel. What I and my colleagues on the Committee\* appointed by the Board of Inland Revenue were more immediately concerned with was the working out of the manipulative details of an operation based on this principle.

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#### XCIV.—*The Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials.*

By T. E. THORPE, C.B., F.R.S.

THE Royal Commission on Arsenical Poisoning, in their First Report, recommended that the Board of Inland Revenue should possess and should exercise powers to specify the ingredients of beer, and the materials used in their preparation which are liable to be contaminated by arsenic, and to prescribe tests by which their freedom from arsenic may be ascertained.

With a view to the carrying into effect of the above recommendation, the Board of Inland Revenue, with the approval of the Treasury, decided to appoint a Committee to advise them as to the tests which might properly be prescribed for the several ingredients of beer which may be held to be liable to contamination.\*

In their Report to the Board, the Committee state that of the various methods which have been suggested from time to time for the detection and estimation of the relatively small quantities of arsenic which may be present in beer and the ingredients of beer, or in the materials which may be used in their preparation, they are of opinion that those methods which depend on the conversion of the arsenic into hydrogen

\* The Committee consisted of :

T. E. Thorpe, Esq., C.B., F.R.S., Principal of the Government Laboratory, as Chairman.

Professor William Augustus Tilden, D.Sc., F.R.S.

Professor Harold Baily Dixon, M.A., F.R.S.

Graham Aldous, Esq.

John Pattinson, Esq., F.I.C., with

Mr. T. J. Cheater, of the Government Laboratory, as Secretary,

arsenide and the subsequent deposition of the arsenic in the elementary form by heating the gas are, on the whole, to be preferred.

The hydrogen arsenide may be formed in practice by the action of so-called "nascent" hydrogen on the arsenic present. The hydrogen may be evolved either electrolytically or through the agency of dilute hydrochloric acid on zinc admixed with, or containing, such an amount of copper or other suitable metal as to give rise to a sufficiently rapid evolution of the gas.\*

The amount of arsenic deposited by heating the hydrogen arsenide so formed is then determined by comparison with deposits obtained in precisely the same manner from wort, beer, malt extracts, sugar solutions, &c., containing known quantities of arsenic.

An electrolytic method for detecting arsenic appears to have been first suggested by the late Professor Bloxam, of King's College (*Quart. Journ. Chem. Soc.*, 1861, 13, 12 and 338), but in its original form it had several disadvantages which have prevented it from being generally adopted by chemists. Modifications of it have been made by Mr. Trotman, Mr. Bevan, and others. The process has been carefully investigated in the Government Laboratory, and in the form now described it is easy of application, and is capable of giving trustworthy results with a comparatively small expenditure of time and trouble.

The apparatus employed in the electrolytic method consists of the following parts :

1. A glass vessel, *A*, provided with a ground-glass stopper and connections, *B*, and a drying tube, *C*, containing calcium chloride.
2. A porous cell, *D*.
3. A glass vessel, *E*.
4. A cooling vessel, *F*.
5. A hard glass constricted tube, *G*.
6. A small Bunsen burner, *H*.

The glass vessel, *A*, forms with the porous vessel, *D*, the inner cell for the cathode where the hydrogen and hydrogen arsenide are produced on passing the electric current. The vessel, *A*, is open at the bottom and fitted at the top with the ground-glass stopper, *B*, through which is passed, to a point just below the neck of the vessel, the stem of the tap-funnel. The glass stopper also carries the gas exit tube on which is a bulb. The tube is bent as shown in the drawing, and is connected by means of a ground-glass joint with the drying tube, *C*. Through the glass cap is fused a stout platinum wire for making the connection on the outside with the current, and within the vessel with the electrode.

The inner electrode, forming the cathode, is of sheet platinum and cone-shaped, with several perforations. It is suspended from a hook made on the end of the wire passing through the glass stopper, and is

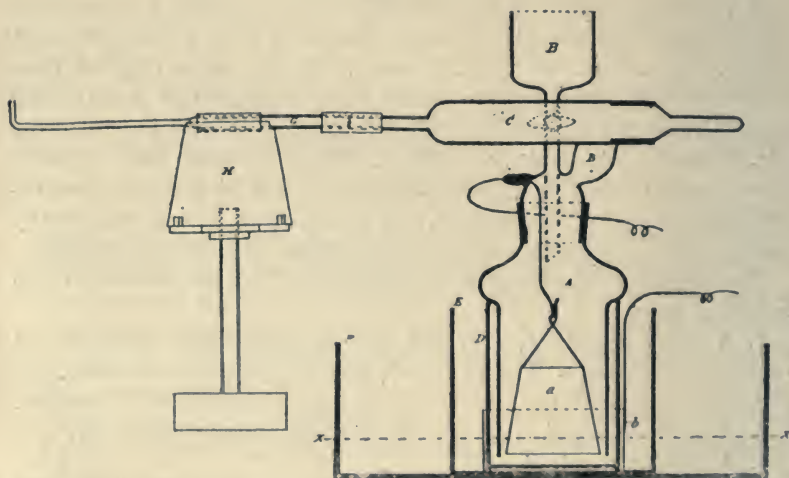
\* In the case of the electrolytic method, it is necessary that the arsenic should be in the condition of an arsenite or arsenious acid.

adjusted so that when the stopper is inserted in the vessel the lower edge of the electrode is 1 mm. above the bottom of the vessel, *A*. It is then securely attached to the wire by closing the hook.\*

The porous vessel, *D*, is larger by 2 to 3 mm. in diameter and in depth than the cylindrical portion of the glass vessel, *A*. As seen in the figure, *A* rests by means of its bulged-out shoulder upon the upper edge of *D*. The porous vessel is of unglazed, highly silicious ware, of the composition employed for the well-known biscuit filters, first made by Dr. Pukal, and is from 1 to 1.5 mm. in thickness.†

The cell for the anode consists of the stout glass vessel, *E*, upon the flat bottom of which the porous vessel, *D*, containing the glass vessel,

FIG. 1.



*A*, stands. The anode consists of a band of platinum, 2 cm. broad, passing loosely round the porous cell, and connected with the current by means of a stout platinum wire. The liquid in the vessel, *E*, should

\* Care must be taken that the hook is effectually closed and the contact complete, otherwise there may be danger of sparking, which might bring about an explosion if the apparatus contained a sufficient proportion of air.

By continued use, the surface of the cathode loses its polish, and the metal becomes coated with a grey powder, especially on the inside of the cone. In these circumstances, the deposit which forms, especially from some saccharine liquids, may retain arsenic. Care should be taken, therefore, that the cathode is re-polished from time to time. After this operation, it is advisable to immerse the cathode completely in the dilute acid and subject it to the action of the current for, say, half an hour.

† The porous vessel may gradually become more or less stained, especially when used with caramels, black beers, and other highly coloured liquids. It is advisable, therefore, from time to time, to heat the vessel in a muffle furnace.



be kept below  $50^{\circ}$ , and the vessel is therefore placed in a larger dish, *F*, containing cold water.

The drying tube, *C*, is packed as follows: A plug of cotton wool is first inserted, and then pure granulated, anhydrous calcium chloride,\* in pieces about the size of small shot or malt grains, for a length of 5 cm. Another loose plug of cotton wool is placed upon the calcium chloride, followed by a roll of lead acetate paper. This is prepared by soaking filter paper in a cold saturated solution of lead acetate and then drying the paper in air. The paper is cut into strips about 1 cm. broad and rolled into a coil fitting loosely in the tube. A small, spiral coil of lead acetate paper is also placed within the enlarged end of the exit tube to which the calcium chloride tube is attached.

To the end of the drying tube, there is fixed by means of a short piece of unvulcanised rubber tubing, the hard glass constricted tube in which the arsenic is to be deposited. The ends of the drying tube and the hard glass tube should be in close contact beneath the rubber. To make one of these tubes, a piece of Jena glass tubing having an external diameter of 5 mm. and an internal diameter of 3.5 mm. is cleaned by successive treatment with acid, water, and alcohol, and dried. It is then held in the blow-pipe flame, so that a portion of the tube about 2 cm. in length and 5 cm. from the end of the tube is thoroughly softened, when the heated portion is drawn out to a length of 7 to 8 cm., and having at a distance of 1 cm. from the shoulder of the tube an external diameter of 2 mm., a size which should be maintained as nearly as possible throughout the length of the constricted part. The tube is cut off near the end of the drawn-out portion, the last 1 cm. of which is turned up at right angles. The hard glass tube is supported in a horizontal position, when attached to the drying tube of the apparatus, by resting in the slots on the upper edge of the cone which surrounds the flame of the small Bunsen burner. A piece of platinum gauze about 2 cm. square is wrapped round the hard glass tube at the point where it is to be heated by the Bunsen flame.

The small Bunsen burner has a circular base 12 mm. high, and its tube is 6 cm. in height and 5 mm. in internal diameter. The upper portion of the tube is threaded and carries a gallery upon which rests a copper cone. The upper edge of the cone contains two slots to receive the hard glass tube.

The apparatus, when employed in the manner to be described, has an apparent resistance of 1.4 ohms, the potential difference between the ends of the wires of the poles being 7 volts with a current of 5 amperes. This strength of current gives about 40 c.c. of hydrogen in

\* Where a series of experiments is carried out with the same apparatus, the calcium chloride should be renewed from time to time, say, after three or four experiments.

a minute, which furnishes a steady flame about 2 mm. in height, and is the strength of current recommended to be used for the purposes of the test. To effect the reduction of the intensity of the main laboratory supply, which is the most convenient source of the current, a rheostat of incandescent lamps may be employed. The lamps are arranged in parallel with each other, but in series with the apparatus, and, according to the current desired, lamps of different candle power may be inserted. An ammeter is included in the circuit.

The apparatus may be arranged for the simultaneous execution of a number of tests. By suitable construction on the charging board, the electric current passes through the solutions arranged in series, and any of these may be brought into or cut out of the circuit as desired. The current is brought to the required strength—4.5 to 5 amperes—by the introduction in the rheostat of lamps of the requisite power according to the number of tests to be carried out simultaneously. A diagram illustrating the method employed for this purpose is shown in Fig. 2 (p. 979).

The sulphuric acid solution employed in the apparatus is prepared by mixing one volume of pure concentrated sulphuric acid with seven volumes of water. It must, of course, be tested to ascertain its freedom from arsenic before it is used.\*

Certain of the solutions to be tested are very liable to froth when introduced into the apparatus. This inconvenience may be obviated by adding one or two c.c. of rectified amyl alcohol (b. p. 128—132°) to the acidified liquid undergoing electrolysis.

Before describing the application of the test, it will be convenient to give in detail the methods to be followed in preparing the extracts or solutions of the various substances in such a form and in such an amount as to render them suitable for testing.

(1) MALT.—Unground malt may readily be examined for arsenic by washing the malt with warm dilute acid and testing the acid extract, but this method is inconvenient in the case of a ground or crushed malt, as it is difficult to obtain a suitable extract. A ground malt is therefore incinerated in presence of lime and magnesia and the solution of the ash tested. Direct experiment has shown that deposits of arsenic obtained after treatment of an unground malt with dilute acid are equal in intensity to those obtained by the basic method of treatment of the same malt. The two methods are as follows :

\* It is advisable to saturate the stock quantity of the dilute acid with the products of its electrolytic decomposition before use in the apparatus. This may be conveniently effected from electrodes of platinum wire immersed in the liquid. The advantage of this procedure is, that it destroys any trace of dissolved sulphurous acid, and thereby obviates the formation of sulphuretted hydrogen during the actual testing.

*Basic Method for Ground Malt.*—Ten grams of the ground malt are transferred to a porcelain, or preferably a platinum, dish about 3

FIG. 2.

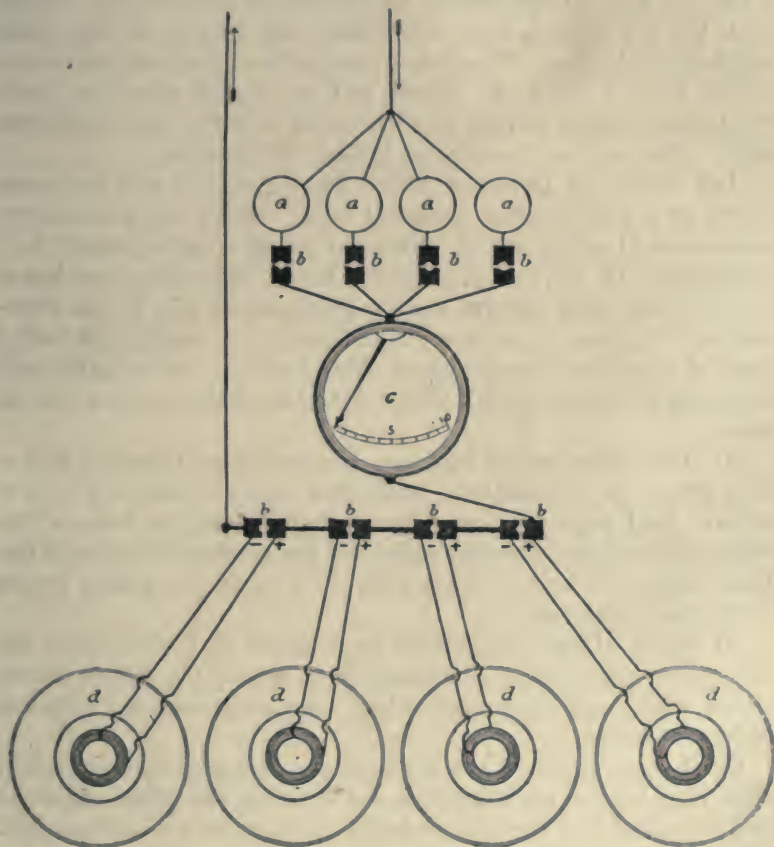


Diagram of the rheostat and charging board arranged for four simultaneous tests. The arrows show the direction of the current.

*a, a, a, a.*—Lamps by means of which the current is reduced to the required strength.

*b, b, b, b.*—Switches.

*c.*—Ammeter.

*d, d, d, d.*—Electrolytic cells as in Fig. 1.

inches in diameter, 30 c.c. of arsenic-free lime water\* are added, and the dish heated over a small Bunsen flame for a few minutes. About

\* The lime-water, lime, magnesia, and potassium metabisulphite are tested as to their freedom from arsenic by the method described under "Chemicals" (pp. 981, 982).



0.5 gram of arsenic-free magnesia or lime is then added and thoroughly mixed with the contents of the dish, the heating of which is continued until the organic matter is completely charred. The dish is then placed in a muffle furnace, or over a low Bunsen flame and heated at a dull red heat until practically all the carbon is burnt off. When cold, the ash is moistened with water and 20 c.c. of the dilute sulphuric acid added. The dish is warmed and the contents transferred to a 4 oz. flask. About half a gram of potassium metabisulphite is added, and the solution boiled until free from sulphurous acid. After cooling, the solution is ready to be tested.

*Acid Method for Unground Malt.*—Forty grams of malt are transferred to a wide-mouthed, stoppered bottle. Forty c.c. of the dilute sulphuric acid and 60 c.c. of water are mixed together, raised to a temperature of 50°, and added to the malt. The bottle is shaken at intervals during 20 minutes and the liquid poured off; 25 c.c., representing 10 grams of malt, are transferred to a small flask, half a gram of potassium metabisulphite added, and the solution boiled until free from sulphurous acid. When cold, the solution is used for the test.

(2) MALT SUBSTITUTES (Glucose, Invert Sugar, Caramel, &c.).—Five grams are weighed in a small flask and dissolved in 20 c.c. of water. Half a gram of potassium metabisulphite and 5 c.c. of the dilute sulphuric acid are then added and the solution boiled until free from sulphurous acid. When cold, it is ready for adding to the electrolytic apparatus.

(3) WORT.—Direct experiments have shown that when using the electrolytic apparatus it is unnecessary to destroy the organic matter of the wort. All the arsenic which may be present is evolved as hydrogen arsenide.

For the test, 25 c.c. of the wort are placed in a small flask, half a gram of potassium metabisulphite and 5 c.c. of the dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid. When cold, the solution is used for the test.

(4) HOPS AND HOP SUBSTITUTES.—Five grams of the substance, ground if necessary in a mortar, are placed in a platinum dish, treated with lime and magnesia and incinerated, and the examination for arsenic carried out in the same manner as described in connection with ground malt.

(5) BEER.—Direct experiments have shown that when the electrolytic apparatus is used it is unnecessary to destroy the organic matter of the beer. All the arsenic which may be present is evolved as hydrogen arsenide.

Twenty-five c.c. of beer are placed in a small flask, half a gram of

potassium metabisulphite and 5 c.c. of dilute sulphuric acid added, and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

(6) YEAST AND YEAST FOODS.—Five grams are introduced into a flask and gently warmed with 20 c.c. of water. Half a gram of potassium metabisulphite and 5 c.c. of dilute sulphuric acid are then added, and the contents of the flask boiled until free from sulphurous acid. The cold solution is used for the test.

Of liquid yeast foods, 25 c.c. are taken and the solution boiled, after the addition of potassium metabisulphite and sulphuric acid, until free from sulphurous acid.

(7) CHEMICALS :

(a) *Sulphites*.—Of solid sulphites, 1 gram is dissolved in 25 c.c. of water in a small flask. Five c.c. of dilute sulphuric acid are added and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

Of solutions of sulphites, 25 c.c. are taken and boiled in like manner after the addition of 5 c.c. of dilute sulphuric acid. The liquid is tested by the addition of a little more sulphuric acid to ascertain if the whole of the sulphite has been decomposed.

(b) *Acids*.—*Sulphuric Acid*.—Five c.c. are diluted with 20 c.c. of water, half a gram of potassium metabisulphite added, and the solution boiled to expel sulphurous acid. When cold, the solution is used for the test.

*Hydrochloric Acid*.—Five c.c. are placed in a porcelain dish and diluted with about 5 c.c. of water. Five c.c. of pure nitric acid (sp. gr. 1.4) and 2 c.c. of pure concentrated sulphuric acid are then added, the dish placed on a sand-bath, and the liquid evaporated until the sulphuric acid fumes. The dish is removed, and, when cold, about 20 c.c. of water and half a gram of potassium metabisulphite added. The solution is transferred to a flask and heated until free from sulphurous acid and then tested.

(c) *Sulphur*.—Ten grams are taken, and the examination for arsenic carried out by burning the sulphur in a current of oxygen in the manner described in connection with the estimation of arsenic in fuel (this vol., p. 969). Owing to the readiness with which sulphur sublimes, the temperature to which the hard glass tube is heated should be as low as possible consistent with the burning of the sulphur, and the empty portion of the hard glass tube, next to the bent and drawn-out end, should not be heated until the sulphur in the other part of the tube has been burnt. The liquid in the absorption tube is boiled to expel sulphurous acid, and any sulphur or other solid substance which may have passed into the absorp-

tion tube in the process of combustion is rendered soluble and in suitable condition for addition to the electrolytic apparatus by the method described for treating the ash of fuel.

(d) *Other Chemicals*.—Of solids, 1 gram is taken and dissolved in 25 c.c. of water. Of liquids, 25 c.c. are taken. In either case, if the solution is alkaline, it must be neutralised by the addition of dilute sulphuric acid. To the neutral liquid, half a gram of potassium metabisulphite and 5 c.c. of dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

8. *FININGS*.—Five grams are weighed out in a flask, 20 c.c. of water added, and gently warmed to effect solution. If sulphurous acid or a sulphite is present, 5 c.c. of the dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid.

If no sulphurous acid is present in the finings, half a gram of potassium metabisulphite is added to the solution prepared as above, together with 5 c.c. of the dilute sulphuric acid, and the solution boiled to expel sulphurous acid and then tested.

#### *Mode of Working.*

The electrolytic apparatus, as already described, is arranged for the test, which is carried out in the following manner. The cells, electrodes, and glass vessel, *A*, with the cap, funnel, and exit tube, are thoroughly cleaned and rinsed with distilled water. The porous vessel, *D*, containing the vessel, *A*, is placed in *E*, which is surrounded by cold water contained in the glass dish, *F*. The calcium chloride tube, *C*, which has been packed in the manner described, is fitted on the ground glass connection. The hard glass tube, *G*, is attached by the indiarubber connection to the drying tube so that the bent portion at the end is in an upright position, and the platinum gauze is so arranged on the tube that it just overhangs the shoulder. The small Bunsen burner, *H*, is placed beneath the tube, which rests in the slots on the upper edge of the cone in such a position that when lighted the flame will heat about 2 cm. of the tube just before the constriction commences.

The connections with the battery wires are made by means of binding screws in such a manner that the current will pass from the vessel, *E*, to the cell, *D*; 30 c.c. of dilute sulphuric acid are then poured into *E*, containing the anode, and 20 c.c. of dilute acid are also run into the cell, *D*, by means of the stoppered bottle, *B*, the stem of which must be left full of liquid.

When all the connections are complete and the acid has been added, the current is switched on and the time noted. At the end of 10 minutes, the apparatus is practically free from air, and the issuing



hydrogen may be lighted. At the same time, the Bunsen burner is lighted and the flame carefully adjusted so that the small piece of platinum gauze is maintained at a red heat throughout the experiment. The heating of the tube during the passing of the gas is continued for 15 minutes, and if, during that time, no brown ring or deposit of arsenic has been formed in the constricted tube (best seen by holding a white card beneath the tube), the apparatus and the acid may be considered free from arsenic and suitable for the application of the test. Two c.c. of amyl alcohol are then run into the inner cell, *D*, by means of the tap-funnel, *B*. This is at once followed by the addition of the solution to be tested, prepared as described, 5 c.c. of water being used for rinsing out the containing vessel. No air must be admitted, and the stem of the funnel must be left full of liquid. If arsenic is present in the added liquid, a deposit begins to form in the narrow tube in the course of a few minutes at a point between 1 cm. and 2 cm. from the heated shoulder. At the end of 30 minutes, the whole of the arsenic, except in very extreme cases, will have been deposited in the tube, which is now sealed up while full of hydrogen. This is effected in the following manner. The stopper of the funnel is opened and a small, pointed flame is at once directed against the narrow tube at a point 3 cm. from the deposit, between the deposit and the turned-up end of the tube, which is meanwhile held by a pair of forceps. The tube at once collapses, and the end is drawn off. The electric current is at the same time disconnected, and then the tube is similarly heated and drawn off just below the shoulder. The deposit of arsenic must on no account be heated by the flame during the sealing of the tube. The short tube, about 4 cm. long, containing the arsenic deposit may then be mounted on white card for reference.

Of course, if the deposit of arsenic thus obtained should be so considerable as to prevent accurate comparison with the standard deposits, the experiment must be repeated upon a smaller quantity of the substance.

*Preparation of the Standard Deposits.*—Although there is good reason to believe that the amount of arsenic deposited is in nowise affected by the nature of the substance with which the arsenic may be associated—0.01 mgm. of arsenic in beer, for example, giving a deposit of equal intensity with the same quantity of arsenic in malt—nevertheless, as the quantitative estimation is based on comparison, it is expedient to make use of deposits prepared by the addition of known amounts of arsenic to arsenic-free specimens of each class of substance. By so proceeding, all doubts which may arise from differences in manipulation or concerning the possible effect of differences in the nature and composition of the substances on the formation of the

deposit are obviated. Thus, for example, in the case of hops and malt, although the final solution to be tested is substantially an acid solution of alkaline earths containing a minute quantity of arsenic, nevertheless, as the malt and hops behave somewhat differently on incineration, and themselves contain different amounts of inorganic matter, it is advisable to make the standards by which malt and hops are to be compared directly from these substances.

The preparation of a solution of arsenic of definite strength for this purpose must be carefully carried out. Pure, resublimed arsenious oxide is ground to a fine powder in an agate mortar and dried at  $100^{\circ}$ . 0.1 gram is accurately weighed on a watch glass and transferred to a litre flask by washing it down a funnel placed in the neck of the flask with 1 or 2 c.c. of pure concentrated hydrochloric acid. The liquid must not be heated. When the solution is complete, it is diluted to 1 litre with distilled water and thoroughly mixed. Each cubic centimetre of this solution (conveniently called *A*) contains 0.0001 gram, or 0.1 mgm. of arsenious oxide. Of this solution, 100 c.c. are carefully measured and transferred to another litre flask and diluted with water to 1 litre. This solution (conveniently called *B*) contains in each c.c. 0.00001 gram (0.01 mgm.) of arsenious oxide.

*Malt.*—It is first necessary to obtain a malt free from arsenic. In certain of the experiments, malt of this character was obtained by drying green malt by means of steam heat. In others, a malt was used which had been dried in cylinders and out of contact with the fumes of fuel. The absence of arsenic in the reagents to be employed must also be ascertained by carrying out a control experiment with the malt, in all respects similar to the actual experiment, but without the addition of arsenic.

Ten grams of arsenic-free malt, previously ground in a mortar, are placed in a porcelain, or preferably a platinum, dish, and 0.2 c.c. of standard arsenic solution *B*, containing 0.002 mgm. of arsenious oxide, is added from a sufficiently narrow burette.\* The whole is then treated in the manner described in connection with the examination of malt, by the basic method. Similar deposits are obtained for 0.004, 0.006, 0.008, 0.010, 0.012, 0.014, 0.016, and 0.018 mgm. respectively.

*Hops and Hop Substitutes.*—A similar series of standards for hops and hop substitutes is prepared by taking 5 grams of hops, previously ascertained to be free from arsenic, adding definite amounts of the standard arsenic solution, and carrying out the method of examination as described in connection with hops.

*Wort and Beer.*—A series of standards is prepared for each of these by adding to 25 c.c. of the measured liquid definite amounts of the

\* The burette used in the experiments had an internal diameter of 7 mm., and 1 cubic centimetre occupied a length of 20 mm.

standard arsenic solution *B*, the liquid being treated in the manner described in connection with the test for wort and beer.

A series of standard deposits is also made for each of the following groups of substances—malt substitutes (glucose and invert sugar), yeast and yeast foods, and chemicals.

*Fuel*.—With regard to the standards for fuel, it has been shown by direct experiments (*v.* "The Estimation of Arsenic in Fuel," p. 969) that all the arsenic which may be present in fuel is obtained by the method described, partly in the hydrochloric acid distillate from the solution of the ash, and partly in the solution containing the arsenic volatilised during combustion; and the amount of arsenic in fuel may be accurately estimated by a comparison of the arsenic deposits obtained by testing the fuel in the prescribed manner with the standards employed in the case of chemicals.

The following table gives the amounts of arsenic, represented by the various standard deposits, converted into grains per pound, or per gallon, or per cwt., according to the nature and amount of the substance tested. In the case of malt, the amount of arsenic in grains per pound is converted into its equivalent in grains per gallon of beer on the assumption that a gallon of beer of the standard gravity 1·055 is produced from 2½ lbs. of malt.

Arsenic deposits obtained from

| Standard<br>$\text{As}_2\text{O}_3$<br>solution. | 10 grams of malt. |  | 25 c.c.<br>of wort,<br>beer, or<br>other<br>liquid. | 5 grams of<br>hops, sugar,<br>caramel,<br>yeast, or<br>other<br>substance. | 1 gram<br>of<br>chemicals. | 10 grams<br>of fuel<br>or<br>sulphur. |
|--|-------------------|--|---|--|----------------------------|---------------------------------------|
| Mgm.   | Grains<br>per lb. | Equal to<br>grains per<br>gallon of<br>beer. | Grains per<br>gallon.                               | Grains per<br>lb.  | Grains per<br>lb.          | Grains per<br>cwt.                    |
| 0·002  | $\frac{1}{150}$   | $\frac{3}{150}$                              | $\frac{1}{150}$                                     | $\frac{3}{150}$  | $\frac{1}{150}$            | 0·15                                  |
| 0·004  | $\frac{2}{150}$   | $\frac{6}{150}$                              | $\frac{2}{150}$                                     | $\frac{6}{150}$  | $\frac{2}{150}$            | 0·31                                  |
| 0·006  | $\frac{3}{150}$   | $\frac{9}{150}$                              | $\frac{3}{150}$                                     | $\frac{9}{150}$  | $\frac{3}{150}$            | 0·46                                  |
| 0·008  | $\frac{4}{150}$   | $\frac{12}{150}$                             | $\frac{4}{150}$                                     | $\frac{12}{150}$   | $\frac{4}{150}$            | 0·62                                  |
| 0·010  | $\frac{5}{150}$   | $\frac{15}{150}$                             | $\frac{5}{150}$                                     | $\frac{15}{150}$   | $\frac{5}{150}$            | 0·77                                  |
| 0·012  | $\frac{6}{150}$   | $\frac{18}{150}$                             | $\frac{6}{150}$                                     | $\frac{18}{150}$   | $\frac{6}{150}$            | 0·93                                  |
| 0·014  | $\frac{7}{150}$   | $\frac{21}{150}$                             | $\frac{7}{150}$                                     | $\frac{21}{150}$   | $\frac{7}{150}$            | 1·09                                  |
| 0·016  | $\frac{8}{150}$   | $\frac{24}{150}$                             | $\frac{8}{150}$                                     | $\frac{24}{150}$   | $\frac{8}{150}$            | 1·24                                  |
| 0·018  | $\frac{9}{150}$   | $\frac{27}{150}$                             | $\frac{9}{150}$                                     | $\frac{27}{150}$   | $\frac{9}{150}$            | 1·40                                  |

The advantages of the electrolytic method are :

1. That it obviates the use of zinc.



2. It is simple in execution, is under perfect control, and may be carried out under such conditions that the results obtained by different operators are strictly comparable, inasmuch as with a current-strength of fair regularity the evolution of the gas is practically constant and uniform.

3. The whole of the solution to be tested for arsenic may be added to the apparatus at once, so that during the whole time of testing the arsenic is under the influence of the "nascent" hydrogen.

4. It has been established that such amounts of arsenic as are present in beer or its ingredients are evolved as hydrogen arsenide during the 30 minutes occupied by the test. The nature of the material associated with the arsenic is found to exercise no inhibiting effect on the formation and evolution of the hydrogen arsenide. Aqueous extracts of malts and worts may be added directly to the electrolytic apparatus without previous destruction of the organic matter as required by the zinc and acid process.

5. The deposits obtained are more uniform in character than those furnished by the zinc and acid method, and admit therefore of more accurate quantitative comparison.

6. The process allows of the simultaneous execution of a number of estimations of arsenic, depending on the arrangement of the rheostat.

The disadvantages of the methods are :

1. The initial cost of the apparatus as compared with that employed in the zinc and acid method.

2. That it can only be applied when an electric current of sufficient intensity is available.

I desire to acknowledge the great assistance I have received from Mr. George Stubbs in working out the details of the method described in this communication.

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XCV.—*A Direct Method for determining Latent Heat of Evaporation.*

By JAMES CAMPBELL BROWN, D.Sc.

IN the course of some investigations on natural fats made a few years ago, it was found desirable to determine the heat of vaporisation of certain aliphatic esters with some degree of accuracy. It soon became apparent that no method hitherto employed was reliable, and at the same time sufficiently convenient for general use. The work accordingly developed into an attempt to find a more satisfactory method, and the results of this inquiry are recorded in the present paper.

The early experimenters, who measured by means of a calorimeter either the heat absorbed during evaporation or the heat evolved during condensation of a known mass of the liquid, obtained discordant figures.

The best and most recent method hitherto employed is that of Marshall and Ramsay (*Phil. Mag.*, 1896, 41, 38). These investigators compared the heat of evaporation of two liquids, one known and the other unknown, by determining the loss of weight in each case when an electric current is passed through a wire immersed in the liquid surrounded by a jacket of its own vapour. This process, which obviates the necessity of knowing the specific heat and of allowing for the heat expended in raising the liquid to the boiling point, is, however, only a comparative method, and besides being attended by difficulties and sources of error is often dependent on the correctness of Griffith's determination of the heat of evaporation of benzene, a constant which was obtained not directly from experiment but by extrapolation from observations made between 20° and 50°.

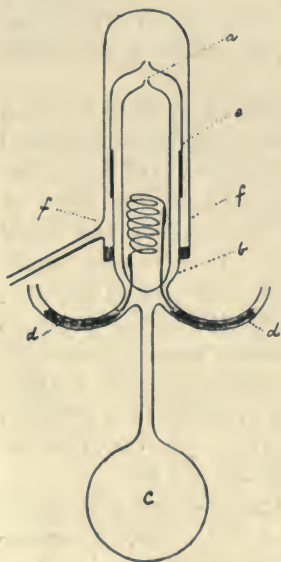
After a number of initial experiments had been made with modifications of Marshall and Ramsay's method, Dr. Ogg, Assistant-Professor of Physics in the University of Aberdeen, suggested that an absolute method might be founded on the following lines. A current of about 1 ampere is sent through a standard resistance coil of about 0.1 ohm, and then through a platinum spiral in a flask or tube containing the liquid. This tube is then placed in a steam jacket containing the vapour of the same liquid at its boiling point (as in Marshall and Ramsay's method). The strength of the current  $C$  is determined by measuring the difference of potential at the terminals  $R_1 R_2$  of the standard resistance :

$$e = Cr \text{ where } r \text{ is known, } \therefore C = \frac{e}{r}$$

The difference of potential  $E$  at the terminals of the platinum

spiral,  $S_1S_2$ , is then measured, and as  $C$  is the same in both cases all the data are thus obtained, the heat developed in the spiral being found from the equation  $C^2R = CE$ , where  $C$  and  $E$  are both known.

Starting with this suggestion, a method has now been worked out which two years' experience has shown to be reliable. With the view of getting as high figures as possible, and thereby obtaining precise readings on the voltmeter, platinoid wire and also the "Beacon" wire of Messrs. Brunton and Son, Musselburgh, were tried, but these are inadmissible for water or acids on account of the chemical changes taking place. Ultimately, platinum wire of the special "C" quality, made by Messrs. Johnson and Matthey, was adopted. The resistance was measured with either a "Weston" or a "Davies" voltmeter very accurately graduated.



The spiral consists of 31 cm. of 0.12 mm. platinum "C" wire, or of 61 cm. of 0.15 mm. wire when sufficient of the substance is available for the larger apparatus; this spiral is welded to terminals of 0.3 mm. platinum wire, and is sealed into a glass tube or bottle of soft German glass approximately 0.5 mm. in thickness, about 10 cm. in length, and 23 mm. in width. This vessel is drawn out, as shown at  $a$  in the figure, to an orifice 1.5 mm. wide, and a loop of platinum wire or glass is fused on to it near the top for conveniently attaching it to the balance when charged. The spiral, which is generally about 35 mm. high, should not occupy more than about one-third of the height of the tube.

The absolutely pure and anhydrous liquid, the latent heat of which is to be determined, is placed in this tube in sufficient quantity to occupy about three-fourths of its volume. The tube is then placed in the expanded neck  $b$  of the peculiarly constructed flask  $c$  in such a way that the thick platinum terminals dip into the mercury in the tubes  $d, d$ ; about 30 to 50 c.c. of the same liquid is placed in the flask  $c$ , which may vary in size according to the quantity of substance available for the experiment. The cap  $e$ , which is ground on to the outside of the neck in the manner indicated, also has a fine orifice at the top.

The glass cover  $f$  is placed over the cap and is fitted tightly by an indiarubber ring placed round the base of the wide neck. This



cover has an exit tube at its lower part connected with a small condenser, which serves to recover the distillate. The liquid in the flask is then made to boil by immersion in a bath, so that its vapour in the inner jacket may heat the spiral tube and its contents to the boiling point. The condensed liquid passes back to the flask and the excess of vapour passes through the orifice in the cap into the outer jacket, warms it also, and so passes to the condenser. The spiral tube, which has first been removed, and allowed to come to the temperature of the room, is weighed, the orifice being always closed by a cap during cooling and weighing; it is then placed in the apparatus and the heat raised and maintained at the boiling point for the same period of time as that required for the final experiment. The tube is again taken out, weighed, and replaced. The loss in weight is the correction required, owing to the escape of any vapour from *a*, and this, although generally very small, is nevertheless appreciable.

The experiment is commenced when the whole interior of the instrument is at the temperature of the boiling point of the liquid. The wires dipping into the mercury tubes *d, d* outside the flask lead to an ammeter and also, by means of a shunt circuit, to a voltmeter, and lastly to a battery of from 2 to 5 secondary cells with a convenient resistance which can be introduced when advisable. The current is now switched on and the time noted. The liquid in the spiral tube must boil immediately if the experiment is to be of any value.

The ammeter is watched, the reading and time being recorded simultaneously about every two minutes; at the same time, the voltmeter is switched into the circuit and the reading recorded. At the end of perhaps 20 minutes the average amperes and volts are calculated. In each experiment, the quantity of substance evaporated by the spiral in 20 minutes varies from 3 to 15 grams.

Preliminary experiments with water and alcohol disclosed the sources of error and indicated what precautions are necessary in using the method. Wire containing iron or nickel is oxidised and hydrogen is liberated. Although too high a temperature in the coil decomposes the liquid and yields permanent gas, yet, on the other hand, the heat produced by the current should be strong enough to cause the liquid to boil immediately on switching on the current. Ultimately four storage cells with a 6-volt glow lamp in the circuit, yielding a current of 0.49 ampere at 3.94 volts, gave the latent heat of steam as 536.8, and four storage cells with no glow lamp in the circuit, yielding a current of 0.96 ampere at 7.74 volts, gave the value 536.4. Another wire coil with 4 cells and a resistance of 3 ohms in the circuit, yielding a current of 0.9625 ampere and 4.61 volts, gave 534.1.

Absolute ethyl alcohol (Kahlbaum) redistilled immediately before

use, with a boiling point of  $78.2^{\circ}$  under 760 mm. pressure, gave the following values for the latent heat:

|        |                        | Amperes. | Volts. | Latent heat. |
|--------|------------------------|----------|--------|--------------|
| 0.005  | { 3 cells current..... | 1.085    | 5.14   | 216.3        |
| wire   | {    "    "    .....   | 1.075    | 5.1    | 216.3        |
| 0.0048 | {    "    "    .....   | 0.7693   | 5.122  | 216.5        |
| wire   | {    "    "    .....   | 0.7833   | 5.106  | 216.5        |

Mean, 216.4

Pure anhydrous ether boiling at  $34.8^{\circ}$  gave the following results:

|       |                            | Amperes. | Volts. | Latent heat. |
|-------|----------------------------|----------|--------|--------------|
| Two   | storage cells.....         | 0.615    | 3.38   | 84.80        |
| "     | " .....                    | 0.620    | 3.40   | 84.72        |
| Three | " (with 2 ohms resistance) | 0.698    | 3.81   | 85.02        |
| "     | " (no additional    "    ) | 0.908    | 5.076  | 84.61        |
| "     | " (    "    "    )         | 0.916    | 5.13   | 84.84        |
| Four  | " (1 ohm    "    )         | 1.066    | 5.837  | 84.76        |
| "     | " (    "    "    )         | 1.074    | 5.946  | 84.68        |

Mean 84.78

$$\begin{array}{ccc}
 & \text{Molecular latent heat} & \\
 \text{at boiling point.} & & \text{at critical point.} \\
 \frac{ML}{T} = 20.33 & & \frac{ML}{\theta} = 13.41
 \end{array}$$

Where  $M$  = molecular weight;  $L$  = latent heat;  $T$  and  $\theta$  = absolute temperatures of boiling and critical points respectively.

Preliminary experiments were made with other liquids in order to find the size of wire and the strength of current which yield the most reliable results with each group of substances with approximately similar boiling points.

The duplicate determinations of the latent heat of the alcohols tabulated below were made with different strengths of current under varying conditions. The samples employed, which were the purest obtainable, were dried and redistilled immediately before being used.

The flask was heated by being immersed either in a warm water-bath, or, for higher temperatures, in melted paraffin, the temperature of the bath being maintained slightly above the boiling point of the alcohol.

To promote the liberation of the vapour, the platinum spiral was

roughened by being covered with platinic chloride and ignited by a current so as to produce a surface of platinum black.

The amyl alcohol determinations were not satisfactory because the inactive sample contained some active constituent; the portion chosen boiled at  $131.6^{\circ}$  and gave  $[\alpha]_D 1^{\circ}$ . The active sample boiled at  $130.1^{\circ}$  and gave  $[\alpha]_D 3.25^{\circ}$  only.

| Boiling point.    | Alcohol.                           | Latent heat.                         |        | $\frac{ML}{T}$ . | $\frac{ML}{\theta}$ . | Latent heat given by other observers.                |
|-------------------|------------------------------------|--------------------------------------|--------|------------------|-----------------------|--|
|                   |                                    |                                      | Mean.  |                  |                       |  |
| 66.2°             | Methyl ..                          | { 262.3<br>262.1<br>262.2 }          | 262.2  | 24.67            | 16.27                 | { 263 (Regnault).<br>261.6 (Marshall<br>and Ramsay). |
| 78.2              | Ethyl.....                         | { 216.3<br>216.3<br>216.5<br>216.5 } | 216.4  | 28.29            | 19.36                 | { 216.5 (Marshall<br>and Ramsay).                    |
| 97.3              | Propyl .....                       | { 166.1<br>166.5 }                   | 166.3  | 26.9             | 18.9                  |  |
| 82.85             | isoPropyl .....                    | { 161.2<br>161 }                     | 161.1  | 27.12            | 19                    |  |
| 116.8             | Butyl.....                         | { 143.3<br>143.2 }                   | 143.25 | 27.14            | 18.9                  |  |
| 108.2             | isoButyl.....                      | { 138.3<br>138.5 }                   | 138.4  | 26.12            | 19.01                 |  |
| 100.2             | sec.-Butyl .....                   | { 136.1<br>136.3 }                   | 136.2  | 26.96            | —                     |  |
| 83°,<br>melts 25° | ter.-Butyl .....                   | { 130.7<br>130<br>130.5 }            | 130.4  | 27.05            | 18.97                 |  |
| 131.6             | isoAmyl (chiefly<br>inactive)..... | { 124.9<br>125.4<br>125.1 }          | 125.1  | 27.1             | 18.97                 |  |
| 130.1             | isoAmyl (chiefly<br>active).....   | { 124.7<br>124.8<br>124.6 }          | 124.7  | 27.17            | —                     |  |
| 176.1             | n-Heptyl .....                     | { 104.8<br>105.2<br>105 }            | 105    | 27.08            | —                     |  |
| 196               | n-Octyl .....                      | { 97.54<br>97.33<br>97.52 }          | 97.46  | 26.97            | —                     |  |
| 180               | sec.-Octyl .....                   | { 94.61<br>94.41<br>94.4 }           | 94.48  | 27.07            | —                     |  |

The acids employed in the determinations tabulated in the following table were dried and redistilled.

Experiments with carefully dried formic acid from various sources gave discordant results, and the sample finally chosen was one specially



prepared by Kahlbaum and transmitted in a sealed tube; this was placed over phosphoric oxide and distilled immediately before use. Three cells with three different resistances were used in the three experiments indicated.

The value of  $\frac{ML}{\theta}$  for butyric acid is probably incorrect, as the critical temperature of  $338^{\circ}$ , calculated by Guldberg, is almost the same as the figure,  $339.9^{\circ}$ , given by Pawlewski for propionic acid.

| Boiling point. | Acid.                     | Latent heat.   |        | $\frac{ML}{T}$ | $\frac{ML}{\theta}$ | Latent heat given by other observers.   |
|----------------|---------------------------|--|--------|----------------|---------------------|---|
|                |                           |  | Mean.  |                |                     |   |
| 101°           | Formic .....              | $\left\{ \begin{array}{l} 120.4 \\ 120.3 \\ 120.4 \end{array} \right\}$          | 120.37 | 14.78          | —                   | $\left\{ \begin{array}{l} 120.4 \text{ (Reg-} \\ \text{nault).} \\ 120.4 \text{ (Marshall} \\ \text{and Ramsay).} \end{array} \right\}$ |
| 117.4          | Acetic .....              | $\left\{ \begin{array}{l} 97.03 \\ 97.12 \\ 96.99 \end{array} \right\}$          | 97.05  | 14.88          | 9.78                | $\left\{ \begin{array}{l} 97 \text{ (Marshall} \\ \text{and Ramsay).} \end{array} \right\}$   |
| 141            | Propionic .....           | $\left\{ \begin{array}{l} 128.9 \\ 129 \\ 128.9 \end{array} \right\}$            | 128.93 | 23.01          | 15.55               |   |
| 163            | Butyric .....             | $\left\{ \begin{array}{l} 113.9 \\ 114 \\ 114 \end{array} \right\}$              | 113.96 | 22.97          | 16.4 ?              |   |
| 154            | <i>iso</i> Butyric .....  | $\left\{ \begin{array}{l} 111.4 \\ 111.4 \\ 111.5 \\ 111.7 \end{array} \right\}$ | 111.5  | 22.94          | —                   |   |
| 184.6          | Valeric, normal..         | $\left\{ \begin{array}{l} 103 \\ 103.1 \\ 103.2 \end{array} \right\}$            | 103.1  | 22.94          | —                   |   |
| 176.3          | <i>iso</i> Valeric ... .. | $\left\{ \begin{array}{l} 101.2 \\ 100.9 \\ 101 \end{array} \right\}$            | 101.03 | 22.9           | —                   |   |

When the esters were being examined, it was considered desirable to compare the results directly with some of the same samples as those used by Marshall and Ramsay. Professor Sidney Young kindly sent me the samples of methyl acetate and methyl propionate which had been used by Marshall and Ramsay; these were dried before use by distillation. The result was in both cases slightly higher, but the difference was small.

| Boiling point. | Ester.                 | Latent heat.  |             | $\frac{ML}{T}$ | $\frac{ML}{\theta}$ | Marshall and Ramsay. | Schiff. |
|----------------|------------------------|---|-------------|----------------|---------------------|----------------------|---------|
| 32.5           | Methyl formate .....   | $\left\{ \begin{array}{l} 110.6 \\ 110.4 \\ 110.4 \end{array} \right\}$ | Mean 110.45 | 21.6           | 13.64               | 110.1                | —       |
| C <sub>3</sub> | Methyl acetate .....   | —   | 98.26       | 22             | 14.18               | 97                   | 93.95   |
|                | (S. Young's)           |   |             |                |                     |                      |         |
| 54.2           | Ethyl formate.....     | $\left\{ \begin{array}{l} 100 \\ 100.2 \\ 100 \end{array} \right\}$     | 100.1       | 22.7           | 14.52               | 94.4                 | 92.15   |
| 78.9           | Methyl propionate:     |   |             |                |                     |                      |         |
| 79             | (S. Young's) .....     | 89.2  | —           | —              | —                   | 89                   | 84.15   |
|                | (Kahlbaum's) .. ...    | 88.8  | —           | 22.22          | 14.6                | —                    | —       |
| 77.3           | Ethyl acetate .....    | $\left\{ \begin{array}{l} 88.18 \\ 88.2 \\ 88.72 \end{array} \right\}$  | 88.37       | 22.16          | 14.67               | 88.1                 | 83.07   |
| 81.2           | Propyl formate .....   | $\left\{ \begin{array}{l} 90.31 \\ 90.28 \\ 90.48 \end{array} \right\}$ | 90.36       | 22.41          | 14.7                | 90.2                 | 85.25   |
| 92.4           | Methyl isobutyrate..   | $\left\{ \begin{array}{l} 79 \\ 79.11 \\ 79.54 \end{array} \right\}$    | 79.07       | 22.03          | 14.73               | 75                   | 75.5    |
| 102.5          | Methyl butyrate.....   | $\left\{ \begin{array}{l} 80 \\ 79.71 \\ 80.5 \end{array} \right\}$     | 79.75       | 21.63          | 14.74               | 79.7                 | 77.25   |
| 99.2           | Ethyl propionate ..    | $\left\{ \begin{array}{l} 80.48 \\ 80.5 \\ 80.37 \end{array} \right\}$  | 80.3        | 22.03          | 14.62               | 81.8                 | 77.1    |
| 102.3          | Propyl acetate.....    | $\left\{ \begin{array}{l} 80.41 \\ 80.5 \\ 80.46 \end{array} \right\}$  | 80.45       | 21.82          | 14.75               | 83.2                 | 77.3    |
| 98.2           | isoButyl formate ...   | $\left\{ \begin{array}{l} 80.54 \\ 80.11 \\ 80.11 \end{array} \right\}$ | 80.12       | 21.98          | 14.8                | —                    | 77      |
| 116.2          | Methyl isovalerate...  | $\left\{ \begin{array}{l} 80.15 \\ 72.5 \\ 72.36 \end{array} \right\}$  | 72.38       | 21.56          | 14.8                | —                    | 69.95   |
| 109.8          | Ethyl isobutyrate ...  | $\left\{ \begin{array}{l} 72.28 \\ 71.97 \\ 71.99 \end{array} \right\}$ | 71.95       | 21.76          | 14.77               | —                    | 69.2    |
| 120.6          | Ethyl butyrate .....   | $\left\{ \begin{array}{l} 71.91 \\ 73.69 \\ 73.72 \end{array} \right\}$ | 73.65       | 21.67          | 14.79               | —                    | 71.5    |
| 122.6          | Propyl propionate ...  | $\left\{ \begin{array}{l} 73.55 \\ 73.84 \\ 73.7 \end{array} \right\}$  | 73.73       | 21.59          | 14.79               | —                    | 71.5    |
| 124.2          | Butyl acetate .....    | $\left\{ \begin{array}{l} 73.65 \\ 73.92 \\ 73.89 \end{array} \right\}$ | 73.9        | 21.6           | 14.79               | —                    | —       |
| 116            | isoButyl acetate ..... | $\left\{ \begin{array}{l} 72.47 \\ 72.28 \\ 72.64 \end{array} \right\}$ | 72.46       | 21.57          | 14.76               | —                    | 69.9    |
| 123.2          | isoAmyl formate.....   | $\left\{ \begin{array}{l} 73.72 \\ 73.81 \\ 73.72 \end{array} \right\}$ | 73.75       | 21.56          | 14.8                | —                    | 71.65   |

| Boiling point. | Ester.  | Latent heat. | $\frac{ML}{T}$ . | $\frac{ML}{\theta}$ . | Marshall and Ramsay. | Schiff. |
|----------------|---|--------------|------------------|-----------------------|----------------------|---------|
| 143·6          | C <sub>7</sub> { Ethyl <i>isovalerate</i> ...           | { 67·85      | 67·84            | 21·6                  | —                    | 64·65   |
|                |   | { 67·76      |                  |                       |                      |         |
|                |   | { 67·92      |                  |                       |                      |         |
|                | Propyl butyrate .....                                   | { 68·28      | 68·29            | 21·27                 | 14·79                | 66·2    |
|                |   | { 68·23      |                  |                       |                      |         |
|                |   | { 68·36      |                  |                       |                      |         |
| 148·4          | C <sub>8</sub> { <i>iso</i> Amyl acetate .....          | { 69         | 69               | 21·58                 | —                    | 66·35   |
|                |   | { 68·92      |                  |                       |                      |         |
|                |   | { 69·07      |                  |                       |                      |         |
|                |   | { 63·3       |                  |                       |                      |         |
| 157            | { <i>iso</i> Butyl <i>isobutyrate</i> .                 | { 63·51      | 63·4             | 21·63                 | —                    | 59·95   |
|                |   | { 64·62      |                  |                       |                      |         |
|                |   | { 64·51      |                  |                       |                      |         |
| 160·6          | { <i>iso</i> Butyl butyrate ...                         | { 64·65      | 64·59            | 21·6                  | —                    | 61·9    |
|                |   | { 65·33      |                  |                       |                      |         |
|                |   | { 65·37      |                  |                       |                      |         |
|                |   | { 65·22      |                  |                       |                      |         |
| 169·4          | { <i>iso</i> Amyl propionate..                          | { 60·43      | 65·31            | 21·66                 | —                    | 63·05   |
|                |   | { 60·32      |                  |                       |                      |         |
|                |   | { 60·47      |                  |                       |                      |         |
| 169·4          | C <sub>9</sub> { <i>iso</i> Butyl <i>isovalerate</i> .. | { 61·79      | 60·41            | 21·54                 | —                    | 57·85   |
|                |   | { 61·86      |                  |                       |                      |         |
|                |   | { 61·72      |                  |                       |                      |         |
|                |   | { 60·53      |                  |                       |                      |         |
| 207·6          | C <sub>10</sub> { <i>iso</i> Amyl butyrate ...          | { 60·39      | 61·79            | 21·57                 | —                    | 59·4    |
|                |   | { 60·53      |                  |                       |                      |         |
| 227            | C <sub>11</sub> { Ethyl caprylate .....                 | { 57·98      | 60·46            | 21·6                  | —                    | —       |
|                |   | { 58·17      |                  |                       |                      |         |
| 227            | Ethyl nonylate .....                                    | { 57·98      | 58·08            | 21·57                 | —                    | —       |
|                |   | { 58·17      |                  |                       |                      |         |

It will be seen that in the same isomeric group the latent heat is lower when the radicle attached to the oxygen atom is the simpler, whilst that attached to the carbon atom is the more complex. Among the esters, as in the case of the alcohols and acids, side chains lower the latent heat of isomerides.

I have to acknowledge my indebtedness to Dr. W. B. Davidson for much assistance in the preliminary work and to Mr. W. H. Roberts, M.Sc., who has carried out most of the final determinations.

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## XCVI.—*Reactions involving the Addition of Hydrogen Cyanide to Carbon Compounds.*

By ARTHUR LAPWORTH.

It is probably a general experience that in preparing cyanohydrins by the addition of the elements of hydrogen cyanide to ketones and aldehydes, the speed of the reaction and the yield of cyanohydrin obtained may vary in an extraordinary manner, even when the experimental conditions are apparently constant. Hitherto, no systematic attempts seem to have been made to discover the cause of the variation, but amongst the records as to the effects of impurities or of slight alterations of the method adopted, the following points appear very significant.

In preparing the cyanohydrins of the aldoses and ketoses, Kiliani found that the addition of a drop of ammonia to the anhydrous hydrogen cyanide was of great assistance (*Ber.*, 1888, 21, 916; and 1889, 22, 370). This effect, however, might have been the result of the usual influence of alkalis in accelerating desmotropic change, and in this case, possibly, the base assisted in the necessary initial formation of the carbonyl modification of the sugar (compare Lowry, *Trans.*, 1899, 75, 214).

Again, it is frequently noticed that hydrogen cyanide is more reactive when it is being produced in presence of the unsaturated compound, and the statement is occasionally made to the effect that only by the use of this process can the addition products be obtained (compare Brecht and Kallen, *Annalen*, 1896, 293, 340). The use of the term "nascent" as applied to such a case, namely, where an electrolyte is being formed by an ordinary double decomposition, is open to serious objection, and, from the standpoint of the electrolytic dissociation hypothesis, is meaningless, for, when once formed in this way, the substance is still nascent in precisely the same sense, that is to say, is being continuously regenerated from its ions.

The whole question being in this unsatisfactory condition, it seemed very desirable that the matter should be more closely examined, attention being particularly directed to the effect produced by small quantities of agents which might not improbably influence the speed of the reactions. There are many difficulties in the way of devising any fairly precise method for the quantitative measurement of the quantities of ketone and aldehyde cyanohydrins formed within definite periods of time, for, owing to the fact that these compounds are undoubtedly dissociated to some extent in solution, any attempt to separate completely the free hydrocyanic acid might lead to the

destruction of a part of the cyanohydrin itself, and the use of silver nitrate or of alkalis is consequently altogether excluded.

It was therefore decided to resort to a method of investigation in which the speed of reaction could be roughly gauged by means of a colour change, and for this purpose, advantage was taken of the fact that camphorquinone has a bright yellow colour, which is perceptible even in very dilute solutions, whilst its cyanohydrin is almost, if not quite, colourless. The use of this substance appeared particularly likely to lead to definite results, as in the original experiments in which the cyanohydrin was prepared in quantity (Trans., 1901, 79, 382) the time of reaction and the yields obtained had been found to vary in an inexplicable manner.

It was anticipated that small quantities of acids, bases, cyanides, and other electrolytes would be likely to produce some noteworthy influence on the velocity of reaction, and the effect of these in particular was investigated, although other possibilities were also tested.

*The Effect of Catalytic Agents on the Velocity of Formation of Camphorquinone Cyanohydrin.*

The quinone was generally used in dilute alcoholic or aqueous solution; excess of freshly distilled hydrocyanic acid was added, and portions of the resulting yellow solution were then transferred to well-stoppered glass vessels; into these were then introduced varying quantities of the agent the effect of which it was desired to ascertain, a record of the time taken for the disappearance of the visible yellow colour being made in each case. With the dilutions usually employed, the colour of the solutions in the absence of foreign substances disappeared in about 8—10 hours.

Mineral acids in small quantities were found to prolong the time occupied to a very marked extent, and with one drop of ordinary hydrochloric acid in 10 c.c. of the solution no noticeable diminution in colour had taken place at the end of 14 days. Small quantities of acetic acid and other weak acids produced a less marked retardation. With large quantities of mineral acids, also, a very great retardation was observed, and no evidence could be obtained after 3 weeks that any cyanohydrin had been formed; this result did not necessarily follow from the similar effect of smaller quantities.

Small quantities of bases, on the other hand, produced a very great acceleration, and one drop of 15 per cent. aqueous potassium hydroxide in 100 c.c. of the yellow solution caused a disappearance of the colour within the space of a few seconds; with a corresponding quantity of ammonia, a less marked effect was noticed, but even here the duration of the action was measured in minutes instead of in hours; the same



remark applies to organic bases like the fatty amines, whether primary, secondary, or tertiary; with the weaker organic bases, such as pyridine, the results again were quite appreciable when comparatively large quantities were used, and they were of the same nature.

With small quantities of neutral salts, such as sodium nitrate or chloride, the effects were very doubtful, but sodium sulphate in large quantity appeared to cause a slight acceleration. With the sodium or potassium salts of weak acids, on the other hand, a marked acceleration was noticed, and substances like borax or sodium phosphate behaved in much the same way as alkalis.

Potassium cyanide produces a great acceleration, but this in itself might be attributed to the effect of the alkaline nature of its solutions. If, however, a solution of camphorquinone cyanohydrin at  $60^{\circ}$  is rendered alkaline by the addition of potassium hydroxide until a faint yellow colour appears, indicating that the cyanohydrin is partially decomposed, and a little powdered potassium cyanide is then introduced, the solution again becomes colourless. Thus, whilst a large concentration of alkali causes the reversal of the reaction, with potassium cyanide this is not the case.

The conclusion to be drawn from the experiments seemed obvious; basic substances act in virtue of the fact that they diminish the concentration of the hydrogen ions, which themselves retard the change. When small quantities of bases or potassium cyanide are present, the concentration of the cyanogen ions must increase, whereas it diminishes in presence of hydrogen ions. It was probable, therefore, that the reaction velocity depended mainly on the concentration of the cyanogen ions, and all subsequent experiments have only served to confirm this view.

The value of the so-called "nascent" as compared with "free" hydrogen cyanide is thus clearly understood; in the latter instance, until the theoretical quantity of strong acid has been added, potassium cyanide is present, and the effect of this would be most marked in cases where the salt is entirely dissolved in the solution containing the unsaturated substance. Doubtless, too, the varying yields obtained in many cases depend on the precise amount of acid introduced; if a little less than the amount required to entirely decompose the cyanide is used, the reaction will continue rapidly; if more, then the velocity will be greatly diminished.

Experiments on other substances have been made in order to test more closely the validity of the above view. The following examples will serve to show that the principle is a fairly general one.



*Condensation of Benzylidenebenzyl Cyanide with Hydrogen Cyanide.*

With the object of preparing considerable quantities of symmetrical diphenylsuccinonitrile, the author, in conjunction with Mr. A. W. Harvey, made a considerable number of attempts to bring about the condensation of hydrogen cyanide with benzylidenebenzyl cyanide in the manner represented by the equation  $\text{CHPh}:\text{CPh}:\text{CN} + \text{HCN} = \text{CHPh}(\text{CN})\cdot\text{CHPh}:\text{CN}$ .

The experiments were performed under a great variety of conditions and at varying temperatures, but without success, and the work was temporarily abandoned. With the knowledge gained in the above investigation of the camphorquinone condensation, the attempt was repeated in the following manner.

Five grams of benzylidenebenzyl cyanide were dissolved in 100 c.c. of alcohol containing 1 molecular proportion of dilute hydrocyanic acid, and the whole heated in a stoppered bottle at  $100^\circ$ ; at the end of 2 hours there was no evidence that any reaction had occurred. A solution of 4 grams of potassium cyanide in 15 c.c. of water was then added, and the heating recommenced; in 5 minutes, rapid separation of a crystalline material commenced, and at the end of half an hour the bottle was cooled, and the solid material collected, washed with alcohol, and finally with ether, which readily dissolves the unaltered benzylidene compound. The crude product presented the appearance of a colourless, crystalline powder, and when dry weighed 2.5 grams; it was found to be a mixture of the  $\alpha$ - and  $\beta$ -diphenylsuccinonitriles, which was analysed without further purification:

0.3021 gave 0.9183  $\text{CO}_2$  and 0.1481  $\text{H}_2\text{O}$ .  $\text{C} = 82.6$ ;  $\text{H} = 5.4$ .

$\text{C}_{10}\text{H}_{12}\text{N}_2$  requires  $\text{C} = 82.8$ ;  $\text{H} = 5.2$  per cent.

$\text{C}_{15}\text{H}_{11}\text{N}$  „  $\text{C} = 87.8$ ;  $\text{H} = 5.4$  „

It is interesting to notice that the same mixture of diphenylsuccinonitriles was made by Challanay and Knoevenagel (*Ber.*, 1892, 25, 289) by warming mandelonitrile with benzyl cyanide and potassium cyanide on the water-bath. Doubtless, this process takes place in the following stages: (1) the reversible decomposition of the mandelic nitrile into benzaldehyde and hydrocyanic acid, (2) the condensation of the benzaldehyde and the benzyl cyanide in the alkaline solution to form benzylidenebenzyl cyanide, (3) the condensation of the latter with the hydrogen cyanide, in presence of the potassium cyanide, to form the dinitrile. Thus, the two methods are in reality the same, but whilst the process of Challanay and Knoevenagel requires 18 hours, when the condensation is carried out in the way above described, it does not occupy more than one hour.

*Condensation of Phorone with Hydrogen Cyanide.*

Anschütz (*Ber.*, 1893, 26, 827) prepared phoronitrile from the unsaturated ketone by first saturating the latter with hydrogen chloride and then boiling the dihydrochloride with potassium cyanide in dilute alcohol. He found that it was necessary to heat the mixture for 18 hours, and that the yield obtained was very uncertain. The following experiments show that no advantage is gained by first preparing the dihydrochloride.

A solution of 10 grams of phorone in alcohol containing 1 molecular proportion of hydrogen cyanide was warmed for an hour at 100°, as in the foregoing experiment, at the end of which time the solution was quite clear. The bottle was therefore cooled, and 1 molecular proportion of potassium cyanide dissolved in a little water was introduced, and the heating then recommenced. A well-defined, crystalline material began to separate within 10 minutes, and increased rapidly in amount; at the end of an hour it was removed, washed with alcohol, and dried. The product, which was nearly pure phoronitrile, weighed 6 grams, and a further quantity was obtained from the mother liquor:

0.3128 gave 0.7170 CO<sub>2</sub> and 0.2337 H<sub>2</sub>O. C = 62.5; H = 8.3.

C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub> requires C = 62.9; H = 8.6 per cent.

The methods above described are not those recommended for the preparation of diphenylsuccinonitrile and phoronitrile, but were made for the purpose of showing that the rapid condensation is not dependent on "nascent" hydrogen cyanide but on the presence of potassium cyanide. It is much more convenient to warm an alcoholic solution of these compounds on the water-bath with an excess of potassium cyanide (1.25—1.5 mols.) dissolved in several times its own weight of water, gradually introducing at the bottom of the mixture 1 molecular proportion of hydrochloric acid by means of a thistle funnel with a very small terminal aperture.

In connection with this method, it should be mentioned that Bredt and Kallen (*Annalen*, 1896, 293, 350) prepared the hydrogen cyanide addition product of ethyl benzyldenemalonate by adding hydrochloric acid to a cold alcoholic solution of the unsaturated ester in presence of potassium cyanide; they also made a number of  $\beta$ -cyano-acids by warming solutions of the esters of alkylidenemalonic acids with potassium cyanide, the cyano-esters being hydrolysed in the process. The esters did not react under other conditions, but the activity of the hydrogen cyanide was erroneously attributed to the circumstance that it was present "*in statu nascendi*."

*The Mechanism of the Hydrogen Cyanide Addition Process.*

The foregoing observations appear to be of considerable value in connection with the theory of the mechanism of the process of the formation of cyanohydrins. The most natural way of expressing the reaction as a whole is



according as it is the hydrocyanic acid itself or its ions which are really concerned.

The extraordinary effect of the cyanide ions at once renders (A) highly improbable, because the hydrogen cyanide being a weak electrolyte is usually present almost entirely in the undissociated form; its amount is increased only to a very slight extent by the addition of small quantities of either strong acids or cyanides, both, it should be observed, decreasing its dissociation. The equation (B) represents a change the velocity of which would be proportional to the product of the concentrations of the ions of the hydrocyanic acid, and this again, in accordance with the general law, is unaltered by the addition of small quantities of acids, bases, or cyanides. Neither view, therefore, can correctly represent the mechanism.

There appears to be only one suggestion which is of any real assistance in this case, and this is one which was made by the author (Trans., 1901, 79, 1267), to account for the commoner types of change among carbon compounds. The suggestion was simply a proposal to extend to carbon compounds the well-known principle\* that ions, and particularly weak ones, frequently unite with neutral components which possess "residual affinity," thus forming complex ions, the process being frequently, if not invariably, a reversible one (compare Abegg and Bodländer, *Zeit. anorg. Chem.*, 1899, 20, 453).

\* The main features of the principle of "complex ions" advanced by Abegg and Bodländer (*loc. cit.*) may be briefly summarised in the following words:

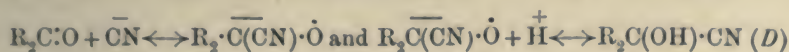
Ions, and more particularly weak ones, may unite with neutral components which possess some form of residual affinity, thus forming complex ions. These appear to have a greater affinity for the electric charge than the simple ions, since it is the latter which, during electrolysis, are liberated at the electrodes in their neutral state, providing, of course, that the concentration of the liquid or the current density is not too great to admit of the sufficiently rapid regeneration of the simple from the complex ions.

In explanation of the greater "electro-affinity" of the complex ion, it is pointed out (*ibid.*, p. 475) that by the distribution of the charge on the simple ion over the larger surface of the former, its potential will naturally be diminished, and therefore the ease with which it is held should now be greater.



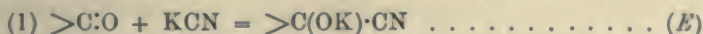
At the present time, it seems more probable than ever that this process may be one of the most important factors in the reactions of carbon compounds, and has been employed in isolated cases by other workers (compare Hantzsch and Schümann, *Ber.*, 1899, 32, 1691).

On this assumption, two possibilities at once present themselves, namely (*C*) that complex ions are formed by the hydrogen ions by union with the ketone or aldehyde, followed by a union of these complex ions with the cyanogen ions, or (*D*) that it is the cyanogen ions which form the initial complex, the two processes being represented by the following diagrams:



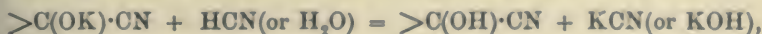
It is easy to show that the law of mass action when applied to the case of (*C*) would predict no acceleration by the addition of a base, but rather the reverse, and this is true whatever may be the relative reaction-velocities of the two stages. In the case of (*D*), however, the predicted results would be precisely those obtained in practice, namely, acceleration by bases and by cyanides of the alkali metals and retardation by acids; if the second stage is very rapid in comparison with the first, it may readily be seen that the velocity will be proportional to the concentration of the cyanogen ions present.

If objection is taken to any ionic view of the change, it may be suggested that the formation of cyanohydrins in presence of potassium cyanide will be represented most satisfactorily as follows:



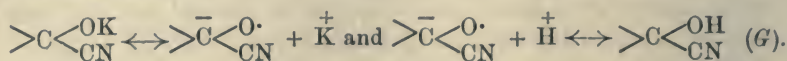
although it should be noticed that this hypothesis does not embrace the whole series of observations described above, as is the case with the explanation previously advanced.

Even if it is admitted that the ions of the cyanide are directly concerned in the change, the view might be held that the reactions could be represented in a simpler manner by supposing that the ionised salt acts in the following way,  $>C:O + K^+ + \bar{CN} = >C(OK) \cdot \bar{CN}$ , but this mode of representing the change would render it necessary to assume the subsequent hydrolysis of this substance, either as in (*F*),

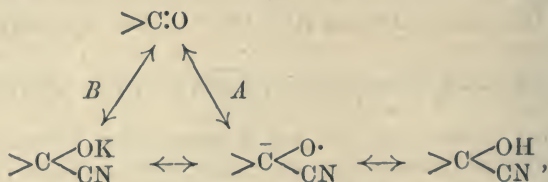


or, in order that this view may possess any claim whatever to recognition as a consistent explanation, the last process must be represented

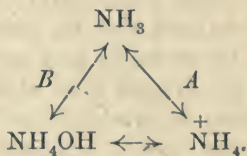
in the usual way as the hydrolysis or double decomposition of the salt of a weak acid,



This hypothesis, which is not less complicated than that put forward above, is one in which the formation of the complex ion is again necessarily assumed. Moreover, this view supplies no clue whatever to the retarding influence exerted by the addition of small quantities of acids, but requires that they should produce no effect. The real difference between the two ionic views is exhibited in the following diagram :



where the reversible reaction, *A*, is assumed in the one case, and *B* in the other. The views differ in the same way as those which may be taken of the formation of an ammonium ion from, say, ammonia and water, namely,



The experiments, therefore, make it appear probable that the formation of cyanohydrins is to be represented as a comparatively slow union of the negative cyanide ions with the carbonyl compound, followed by the almost instantaneous combination of the complexes with hydrogen ions. This was *a priori* the most probable mode of viewing the mechanism, as had been previously pointed out (Trans., 1901, 79, 1268), where the exactly inverse process was suggested in alluding to the disruption of acetone cyanohydrin by alkalis.

If, then, hydrogen cyanide addition reactions are thus to be explained, it should follow, where the addition product is not easily decomposed by alkali, that, in the presence of water to provide the hydrogen ions, potassium cyanide itself in sufficiently concentrated solution should be capable of effecting the conversion.

The following experiments were therefore made in order to test this conclusion.

*Action of Potassium Cyanide on Aldehydes, Ketones, and  $\alpha\beta$ -Unsaturated Ketones and Nitriles.*

(a) *Camphorquinone*.—The quinone (5 grams) was dissolved in ether and shaken with a moderately strong cold solution of potassium cyanide (10 grams). The yellow colour rapidly diminished in intensity, and when no further alteration was apparent, the ethereal solution was removed, washed repeatedly with water, dried over calcium chloride, and evaporated by means of a current of air, the residual yellow mass being treated with fuming sulphuric acid in the method recommended in a previous paper (Trans., 1901, 79, 382). The colourless, microcrystalline, crude product, which, when dry, weighed about 1.5 grams, had all the properties of a mixture of the amides of the  $\alpha$ -hydroxycamphorcarboxylic acids, and on crystallisation from acetone gave the pure amide melting at 235–240°:

0.2802 gave 0.6419  $\text{CO}_2$  and 0.2105  $\text{H}_2\text{O}$ .  $\text{C} = 62.3$ ;  $\text{H} = 8.3$ .

$\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 62.6$ ;  $\text{H} = 8.1$  per cent.

(b) *Benzaldehyde*.—Twenty grams of the aldehyde were shaken with 20 c.c. of water containing phenolphthalein, and sodium hydroxide was added until the water showed a permanent alkaline reaction. A solution containing 45 grams of potassium cyanide in 150 c.c. of water was then added, and the shaking continued for 2 minutes; after this the whole was left until a separation into two layers occurred, when the clear oil was removed and shaken repeatedly with large quantities of water rendered faintly alkaline with sodium hydroxide, when it was removed, dissolved in ether, and dried over calcium chloride. The product thus obtained was boiled with strong hydrochloric acid and worked up for mandelic acid in the usual way. The acid, recrystallised from benzene, weighed 3 grams and melted at 116–117° (pure mandelic acid melts at 118°). A larger quantity could probably have been obtained, as a considerable amount of material was rejected during the purification.

(c) *Benzylidenebenzyl Cyanide*.—Five grams of benzylidenebenzyl cyanide dissolved in dilute alcohol containing 5 grams of potassium cyanide gave 1.8 grams of the mixed diphenylsuccinonitriles after 20 minutes' heating on the water-bath.

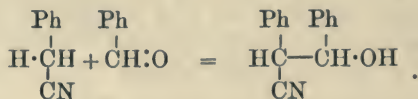
(d) *Phorone*.—Five grams of phorone warmed on the water-bath with 10 grams of potassium cyanide dissolved in dilute alcohol gave 3.9 grams of the pure nitrile after 45 minutes.

Although it is impossible to bring potassium cyanide and water together without producing some free hydrocyanic acid, it was, nevertheless, thought necessary to make the above experiments.

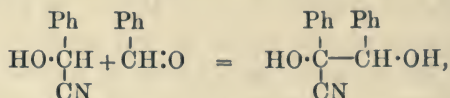


*The Benzoin Reaction.*

It is now generally accepted that the condensation of ketones and aldehydes with compounds such as ethyl malonate, acetoacetate, benzyl cyanide, and in general such substances as contain the grouping  $>\text{CH}\cdot\text{R}$  (where  $\cdot\text{R}=\cdot\text{CO}\cdot, \cdot\text{NO}_2, \cdot\text{CN}, \cdot\text{SO}_2\cdot$ ) is the result of an additive process in which a hydroxy-compound is produced, as, for example :



Now it has been shown that the first product of the action of potassium cyanide on benzaldehyde is mandelonitrile (=hydroxybenzyl cyanide). The former, like benzyl cyanide itself, has a labile  $\alpha$ -hydrogen atom and in the alkaline solution would condense with benzaldehyde as follows :



which is simply the unstable cyanohydrin of benzoin,  $\begin{array}{c} \text{Ph} \quad \text{Ph} \\ | \quad | \\ \text{O}\cdot\text{C}-\text{CH}\cdot\text{OH} \end{array}$ ; this would break up, reversibly, into benzoin and hydrogen cyanide, which would then be available for a further conversion of the benzaldehyde.

To test this latter view, 10 grams of benzaldehyde were converted into mandelonitrile in the usual way, and washed with water repeatedly; the oil was then mixed with 10 grams of freshly distilled benzaldehyde, and 3 grams of tripropylamine were added to the mixture. After remaining at the temperature of the laboratory for 20 days, the material, which had been converted into a semi-solid, yellow mass and had evolved hydrocyanic acid continuously, was triturated in a mortar with dilute alcohol containing hydrochloric acid in order to remove the base, and was then washed repeatedly with water and dissolved in a small quantity of alcohol. A yellow, crystalline material separated; this weighed 4 grams, and was easily identified as benzoin by its melting point, crystalline form, and behaviour with pure benzil and alcoholic potassium hydroxide (Bamberger and Scholl, *Ber.*, 1899, 32, 1809) :

0.3018 gave 0.8733  $\text{CO}_2$  and 0.1589  $\text{H}_2\text{O}$ .  $\text{C}=78.9$ ;  $\text{H}=5.8$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2$  requires  $\text{C}=79.2$ ;  $\text{H}=5.7$  per cent.

In conclusion, it may be pointed out that the additive reactions of

hydrogen cyanide occur under the same condition as those of ethyl malonate, ethyl acetoacetate, and similar compounds. The mechanism is doubtless much the same in all these cases, and of course affords no clue to the constitution either of the free compounds or of their metallic derivatives. Moreover, in connection with this point, the experiments described in the preceding pages do not exclude the possibility that in certain circumstances, particularly in the absence of much water, or in solvents such as ether or benzene, the additive reactions might occur under the influence of powerful acids, but in such cases, doubtless, the mechanism is of a different character.

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### XCVII.—*Resolution of $\alpha$ -Benzylmethylacetic Acid.*

By FREDERIC STANLEY KIPPING and ALBERT EDWARD HUNTER.

WISHING to obtain an optically active acid from which an optically active acid chloride might be prepared, for various purposes to be described in future communications, the authors first turned their attention to *d*-mandelic acid, and attempted to convert it into *l*-phenylchloroacetyl chloride,  $C_6H_5 \cdot CHCl \cdot COCl$ , as described in the case of *l*-mandelic acid by Walden (*Ber.*, 1895, 28, 1295); the results, however, were not satisfactory, because, owing to the high temperature at which alone the alcoholic hydroxyl group is displaced by chlorine, the product was sometimes optically inactive, and it was a very difficult, if not an impossible, task to prevent partial racemisation from taking place, the specific rotation being usually about one-fifth of that given by Walden for the pure substance.

In these circumstances, it became necessary to obtain some other optically active monocarboxylic acid, which might be more suitable for the end in view, and experiments were commenced on the resolution of benzylmethylacetic acid or  $\alpha$ -methylhydrocinnamic acid, a compound which is very easily prepared in large quantities and at a moderate cost.

The results of these experiments were in all respects satisfactory; the acid is resolved without difficulty when its quinine salt is fractionally crystallised, and the *d*-acid, which is thus obtained, can be converted into the active chloride at relatively low temperatures, so that racemisation is almost entirely prevented.

*Resolution of the Acid.*

The benzylmethylacetic acid,  $C_6H_5 \cdot CH_2 \cdot CH(CH_3) \cdot CO_2H$ , used in these experiments was prepared by heating either ethyl benzylacetate with methyl iodide or ethyl methylacetate with benzyl chloride, both condensations being effected in the presence of sodium ethoxide; the product in either case was subsequently hydrolysed with concentrated alcoholic potash; the crude acid was then purified by distillation under reduced pressure, and thus obtained as an oil boiling at  $160^\circ$  under 12 mm. pressure; its purity was established by an analysis of its silver salt:

0.129 gave 0.0515 Ag; Ag = 39.9.

$C_{10}H_{11}O_2$  Ag requires 39.88 per cent.

The resolution of the acid may be accomplished by fractionally crystallising its quinine salt from water or alcohol; in the first case, the acid (1 mol.) and the quinine (1 mol.) are placed together in a large beaker, and steam is blown into the liquid until nearly all the oily salt has dissolved, the clear solution is then quickly decanted whilst hot from some resinous matter which is invariably present, allowed to cool, and the colourless deposit which consists of minute prisms repeatedly crystallised in a similar manner.

Owing to the large volume of water (about a litre for 20 grams of salt) required for each operation, this method was found to be somewhat troublesome, and the following was adopted.

The acid in portions of 25 grams is mixed with twice its weight of quinine, and the mixture then warmed with 50—75 c.c. of purified methylated spirit until it has dissolved; the solution is then placed aside, allowed to cool slowly and completely, and the crystalline deposit collected at the pump.

It is important to note that the solution should not be stirred during cooling, or filtered before it is quite cold, otherwise the salt is deposited in such a very fine state of division that it is only with difficulty separated from the mother liquors.

The first deposits are collected and recrystallised from hot alcohol, in which the salt is very readily soluble, until the melting point of the dried compound has risen to  $119$ — $120^\circ$ ; this usually requires 3 or 4 operations, but their number obviously depends on the concentration



and on the relative quantity of salt contained in each deposit: the last portions of the mother liquors are best removed at each filtration by washing with ether, in which the salt is practically insoluble. Ethyl acetate may also be used for crystallising the salt, which is not so soluble in this liquid as in alcohol, and separates from it in well-defined crystals. In systematic experiments, 240 grams of acid yield without difficulty an approximately equal weight of pure quinine salt, corresponding with about 80 grams of *d*-acid; on further evaporation, the mother liquors give deposits of the crude salt of the *d*-acid, and after filtration they can be worked up for crude *l*-acid.

Quinine *d*-benzylmethylacetate,  $C_{20}H_{24}N_2O_2 \cdot C_{10}H_{12}O_2$ , crystallises from hot alcohol in which it is very readily soluble in long, slender prisms; it is readily soluble in boiling ethyl acetate, but only very sparingly so in boiling water, and practically insoluble in cold ether. It melts at  $119-120^\circ$  when previously dried at  $100^\circ$ , but a trace of moisture depresses the melting point several degrees.

Many determinations of the specific rotation of the salt have been made in order to test its purity; the following results were obtained with samples which had been recrystallised about ten times and until the specific rotation underwent no further change; a 200 mm. tube was used in each case.

| Substance. | Solvent.      | Volume of solution. | $\alpha_D$ .  | $[\alpha]_D$ . |
|------------|---------------|---------------------|---------------|----------------|
| 0.5 gram   | Ethyl acetate | 25 c.c.             | $-3.05^\circ$ | $-76.2^\circ$  |
| 0.5 "      | Ethyl alcohol | "                   | 4.45          | 111.2          |
| 0.5 "      | "             | "                   | 4.5           | 112.5          |

Owing to the relatively low specific rotation of the acid, the change in specific rotation of the salt with increasing purity is comparatively small, and the melting point is almost as good a criterion of purity as optical examination.

#### *d*-Benzylmethylacetic Acid.

The acid obtained by decomposing the quinine salt with dilute sulphuric acid and extracting with ether remains as a colourless oil when the dried ethereal solution is evaporated, and does not crystallise when kept for a long time at the ordinary temperature.

As it seemed inadvisable to submit it to distillation owing to possible racemisation, it was simply left in a vacuum for a few days over concentrated sulphuric acid, and then examined optically. Various samples which were thus prepared, when examined (without solvent) in a 100 mm. tube, gave  $\alpha_D +20.26^\circ$ ,  $+19.0^\circ$ , and  $+20.0^\circ$ ; from these concordant results, it might be concluded that the acid was free from its *l*-isomeride.

In order to ascertain whether this was really the case, a sample was converted into its sodium salt, and the latter was fractionally precipitated by adding ether to its solution in methyl alcohol; the sodium salt thus obtained in lustrous plates seemed homogeneous, and the second and third fractions were examined, after drying at  $100^{\circ}$ , using a 200 mm. tube.

| Substance.  | Solvent. | Volume of solution. | $\alpha_D$ . | $[\alpha]_D$ . |
|-------------|----------|---------------------|--------------|----------------|
| II 0.5 gram | Water    | 25 c.c.             | + 1.04       | + 26°          |
| III 0.5 "   | "        | "                   | 1.04         | 26             |

The pure sodium salt was then dissolved in water and the solution treated with a slight excess of quinine hydrochloride, the precipitate of quinine *d*-benzylmethylacetate which was produced was recrystallised, first from alcohol and then from ethyl acetate, and thus obtained in the usual form, melting at  $119-120^{\circ}$ .

0.5 gram of this preparation, dried at  $100^{\circ}$ , dissolved in ethyl alcohol, the solution made up to 25 c.c., and examined in a 200 mm. tube, gave  $\alpha_D - 4.42^{\circ}$  and  $[\alpha]_D - 110.5^{\circ}$ ; this result seems to prove that the original acid (+  $20^{\circ}$ ) is the pure *d*-compound. The alcoholic mother liquors obtained in fractionating the quinine salt were worked up for crude *l*-acid; the oil thus obtained gave, when examined in a 100 mm. tube without solvent,  $\alpha_D - 10^{\circ}$  to  $-12^{\circ}$ , and consists of about 75 and 25 per cent. of the *l*- and *d*-acids respectively; attempts to prepare the pure *l*-acid from this substance by fractionally crystallising the sodium salt or the copper salt from water or alcohol were not successful.

#### *d*-Benzylmethylacetyl Chloride.

*d*-Benzylmethylacetic acid is readily acted on by phosphorus pentachloride at the ordinary temperature, and after heating at about  $60^{\circ}$  under reduced pressure, the chloride remains as an almost colourless oil with a very disagreeable odour; when distilled under 15 mm. pressure, it boils at  $120-121^{\circ}$ .

Various samples thus prepared were examined in dry ethereal solution:

| Substance. | Volume of solution. | Length of tube. | $\alpha_D$ . | $[\alpha]_D$ . |
|------------|---------------------|-----------------|--------------|----------------|
| 2.0 grams  | 25 c.c.             | 200 mm.         | + 2.44°      | + 15.25°       |
| 8.5 "      | "                   | "               | 10.56        | 15.5           |
| 4.5 "      | "                   | 100 mm.         | 3.4          | 18.0           |

From these fairly concordant results it might be inferred that the acid chloride does not undergo racemisation, but in one or two experiments the distilled product was found to be optically inactive. In order to ascertain the conditions of this racemisation, a sample of *l*-acid, having  $[\alpha]_D - 7.5^{\circ}$  in ethereal solution, was converted into

chloride, the latter slowly distilled under 15 mm. pressure, and then hydrolysed with cold water; the recovered acid, when examined in ethereal solution, was practically inactive.

A sample of the same acid ( $[\alpha]_D - 7.5^\circ$ ) was then converted into its chloride, the phosphorus oxychloride removed by heating at  $60^\circ$  in a vacuum, and the residual chloride hydrolysed with cold water; the acid thus obtained gave, in ethereal solution,  $[\alpha]_D - 6.0^\circ$ , so that there was no very great change in its optical properties.

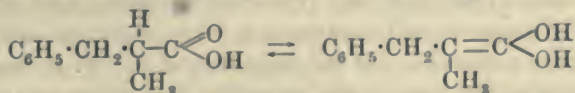
It appears from these experiments that the racemisation is caused by distilling the chloride, and not by the action of the phosphorus pentachloride; an experiment made with some pure *d*-acid, as follows, confirmed this conclusion.

3.5 grams of the pure *d*-acid ( $[\alpha]_D + 22.6^\circ$ ) in light petroleum solution were treated with the theoretical amount of phosphorus pentachloride, and the mixture kept for one hour, during which time the reaction proceeded very gently; the light petroleum was then distilled off under 15 mm. pressure and the residue heated at  $60^\circ$  under the same pressure for one hour in order to volatilise the phosphorus oxychloride; the residual acid chloride, when examined optically in light petroleum solution, gave  $[\alpha]_D + 25.5^\circ$ . The light petroleum was then distilled off under reduced pressure and the acid chloride heated at  $70^\circ$  under 15 mm. pressure for one hour; when brought into solution again by means of the same solvent, it was found that the rotation had fallen to  $[\alpha]_D + 23.0^\circ$ .

The acid chloride, after evaporating the solvent, was heated at  $90^\circ$  for half an hour under 30 mm. pressure; on examination, it was found that the specific rotation was  $+11^\circ$ , and when the chloride was again heated at  $100$ — $110^\circ$  for about 15 minutes under atmospheric pressure, it was almost completely racemised, the solution in light petroleum, when made up to 20 c.c., giving  $[\alpha]_D + 2^\circ$ . This seems to show that the acid chloride is unstable when heated, partial racemisation taking place even at  $70^\circ$ .

#### *Experiments on the Racemisation of the Acid.*

Although the acid chloride undergoes racemisation at comparatively low temperatures, experiments made with the *d*-acid show that this compound exhibits remarkable stability in this respect; it might be thought, from the fact that the asymmetric grouping is in the  $\alpha$ -position with respect to the carboxylic group, that the change



would readily take place, but such does not seem to be the case.



A small quantity of the *d*-acid was dissolved in methyl alcohol; the solution, which gave a rotation of  $+0.69^\circ$  in a 200 mm. tube, was then boiled under a reflux condenser for 4 hours, but the rotation underwent no change; the solution was then heated in a sealed tube at  $170^\circ$  for 2 hours, but, on examination, no decrease in its action on polarised light could be detected.

Having obtained a considerable quantity of impure *l*-acid, attempts were made to separate the pure *l*-compound from the *d*-acid present; these, however, proving unsuccessful, the acid was distilled under reduced pressure, and afterwards under atmospheric pressure, in the hope of racemising it, but the optical activity was found to be approximately the same as before.

The authors desire to express their gratitude to the Government Grant Committee of the Royal Society for a grant in aid of this research.

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### XCVIII.—*Notes on Ozone. Estimation, Solubility, and Interaction with Hydrogen Peroxide.*

By JOHN KENNETH HAROLD INGLIS, M.A., B.Sc., 1851 Exhibition Scholar.

THE experiments of Ladenburg (*Ber.*, 1901, 34, 1184) have shown that ozone can be accurately estimated by means of its action on potassium iodide in *neutral* solution, the solution being acidified *after* the action is complete. In this case, a molecule of iodine is formed for each molecule of ozone present. If, however, the ozone acts on an acidified solution of potassium iodide, the amount of iodine set free is greater than would correspond with this ratio; for in this case if the iodide is very dilute three atoms of iodine are formed for each molecule of ozone. Now it has been shown that ozone forms some complex when dissolved in acids (*Zeit. physikal. Chem.*, 1903, 43, 229), and it was thought that the nature of this complex could be determined by a study of the solubility of ozone in water and acids. The object of these experiments was (1) to find a reliable method for the estimation of ozone in acid solution and (2) to study the solubility of ozone in water and acids. At the suggestion of Sir W. Ramsay, some further experiments were made regarding the action of ozone on hydrogen peroxide.

### I. *Estimation of Ozone in Acid Solution.*

When these experiments were begun, no data for the estimation of ozone in acid solution had been published. But in a recent paper Ladenburg (*Ber.*, 1903, 36, 115) has shown that ozone can be estimated in acid solution by means of its action on sodium hydrogen sulphite and on arsenious acid. The results obtained by Ladenburg show, however, considerable variation, so that further work on the subject seemed desirable.

Since the extra amount of iodine formed in acid solution was probably due to the hydriodic acid being too easily oxidised by the ozone, it seemed likely that a less easily oxidisable substance, such as hydrobromic acid, would give more regular results. As it was possible that the action of ozone gas on hydrobromic acid would not be the same as that of an acid solution of the gas, Ladenburg's method could not be directly employed. Hence, in order to ascertain the amount of ozone taken the following procedure was adopted. A solution of ozone in water was prepared and equal volumes (50 c.c.) were added to 10 c.c. of (1) water, (2) an acid. To No. 1, potassium iodide was added, followed by a small quantity of acid; to No. 2, potassium bromide, and then, after a short time, potassium iodide. The iodine liberated was then titrated with  $N/100$  sodium thiosulphate, and in this way the same amount of ozone was estimated by means of Ladenburg's method and by means of potassium bromide in acid solution. The water and acid used in these experiments were first of all treated with ozone to destroy any oxidisable matter, and then boiled to drive off the remaining ozone. Usually, five estimations were carried out together, the first and last according to Ladenburg's method and the remaining ones by the bromide method. Table I (p. 1012) shows the number of c.c. of thiosulphate required in each case.

A solution of ozone in  $N\text{-HNO}_3$  gave the following figures:

- (a) Estimation with iodide (in acid solution), 8.75 c.c. and 8.70 c.c.
- (b) Estimation with bromide, 6.30 c.c., 6.40 c.c., 6.45 c.c.

These figures show that the iodide method gives a high result with an acid solution of ozone, and also that the estimation by means of bromide does not give very concordant results; but although every precaution was taken in order to increase the accuracy a closer agreement could not be obtained. Now, the differences between the iodide titres of Table I are not much less than those between the other three titres, and they are all probably due to experimental error, which is unavoidably high owing to the method which has to be adopted. Hence, the conclusion may be drawn that ozone in acid solution acts on potassium bromide according to the equation  $\text{O}_3 + 2\text{HBr} = \text{Br}_2 + \text{O}_2 + \text{H}_2\text{O}$ .

TABLE I.

| Potassium<br>iodide.<br>neutral. | Potassium bromide in acid solution.      |       |       | Potassium<br>iodide<br>neutral. |
|----------------------------------|--|-------|-------|---------------------------------|
|                                  | Acid.                                    | 1.    | 2.    | 3.                              |
| 10.50                            | <i>N</i> -H <sub>2</sub> SO <sub>4</sub> | 10.13 | 9.87  | 9.58                            |
| 9.00                             | <i>N</i> -H <sub>2</sub> SO <sub>4</sub> | 8.65  | 8.80  | 8.65                            |
| 11.95                            | <i>N</i> -HNO <sub>3</sub>               | 12.05 | 12.30 | 12.07                           |
| 13.10                            | <i>N</i> -HNO <sub>3</sub>               | 13.40 | 12.80 | 13.10                           |
| 13.00                            | <i>N</i> -HNO <sub>3</sub>               | 12.05 | 12.05 | —                               |
| 12.85                            | <i>N</i> -HNO <sub>3</sub>               | 12.30 | 11.80 | 11.50                           |
| 12.65                            | <i>N</i> -HNO <sub>3</sub>               | 12.40 | 12.20 | 12.15                           |

II. *Solubility of Ozone.*

In some experiments carried out by Schöne (*Ber.*, 1873, 6, 1224), it was shown that when ozonised oxygen was passed through distilled water a true equilibrium was not reached since, although the concentration of the dissolved ozone remained constant, the gas did not pass through the solution unchanged, one-fourth of the ozone being decomposed into oxygen. Schöne applied this result to correct Carius' determination of the solubility, not realising that in such a case there can be no question of a solubility, since the apparent solubility would depend on the rate of passage of the gas. It seemed advisable, therefore, to repeat Schöne's experiments in order to decide whether the solubility could be used to ascertain what complex is formed by the ozone in acid solution.

The method employed was as follows: pure dry oxygen, prepared from potassium permanganate, was passed through an ozoniser and thence through (1) a bulb fitted with two taps and having a capacity of 80 c.c.; (2) a gas-washer containing distilled water; (3) a phosphorus pentoxide tube; (4) a second bulb similar to (1). The gas-washer contained a spiral through which the ozone was bubbled,



this arrangement ensuring good stirring and thorough contact of the gas with the solution. The ozone was passed through the apparatus until the concentration of the ozone in the gas-washer was constant. The taps on the two bulbs were then closed, the apparatus disconnected (the different parts were connected by ground glass joints), and the contents of the two bulbs were then analysed by aspiration into neutral potassium iodide, &c., as in Ladenburg's method. If no decomposition had taken place during the passage of the ozone through the solution, the contents of the two bulbs should give identical results on analysis. In order to be certain that any differences found were caused by the action of the water and not by that of the connecting tubes or the phosphorus pentoxide, similar experiments were made in which the gas-washer was omitted. The results are given in Table II.

TABLE II.

|                                       | Gas-washer used. |      |      |      | Gas-washer omitted. |      |
|---------------------------------------|------------------|------|------|------|---------------------|------|
|                                       |                  |      |      |      |                     |      |
| Percentage of ozone in first bulb ... | 10.5             | 12.7 | 11.4 | 11.8 | 8.67                | 6.00 |
| Percentage of ozone in second bulb... | 9.9              | 12.1 | 10.5 | 10.1 | 8.29                | 5.84 |

The above results confirm Schöne's experiments and indicate that ozone, when passed through water, is partly decomposed. Hence there can be no question of the solubility of ozone in water, and it is therefore impossible to study the molecular state of dissolved ozone by means of its solubility relationships.

### III. *Interaction of Ozone and Hydrogen Peroxide.*

Ever since the time of Schönbein (see Dammer, *Handbuch der anorg. Chem.*, Vol. I, p. 434) it has been believed that ozone and hydrogen peroxide mutually destroy one another. Now the odour of ozone is not destroyed by passing it through hydrogen peroxide, and it has been stated recently (*Ber.*, 1902, 35, 2905) that the substances have no action on one another. Sir W. Ramsay suggested to me that the action might possibly be a slow one, and that by mixing solutions of the two substances the rate of their reaction might be determined. A solution of ozone in water was therefore prepared, and equal portions (50 c.c.) were placed in a series of flasks. Each of these was treated with 5 c.c. of a dilute hydrogen peroxide solution (5 c.c. = 14.2 c.c. of  $N/50\text{-KMnO}_4$ ), and then, after different intervals of time, dilute sulphuric acid was added and the amount of unchanged peroxide was estimated by means of permanganate solution, which has no action on ozone.

TABLE III.

| Time .....              | 5 minutes. | 20 minutes. | 36 minutes. | 50 minutes. |
|-------------------------|------------|-------------|-------------|-------------|
| Permanganate used ..... | 11.2 c.c.  | 12.2 c.c.   | 12.6 c.c.   | 12.65 c.c.  |

These figures would seem to indicate that the amount of peroxide decomposed diminishes as the time increases, but the true explanation is as follows. Although ozone has no action on permanganate, it oxidises a manganous salt to the dioxide, and this dioxide is easily reduced by hydrogen peroxide. Now the permanganate used was so pure that it had no action on pure hydrogen peroxide until a small quantity of manganous sulphate was added (*Zeit. Elektrochem.*, 1903, 9, 226). Hence, during the titration, the manganous salt would act catalytically on the ozone and hydrogen peroxide and so diminish the number of c.c. of permanganate required, and as some of the ozone would undoubtedly slowly escape, the catalytic action, and therefore the apparent amount of decomposition of the peroxide, would diminish as the time increased. As a confirmation of this explanation, it was found that if manganous sulphate was added at once to the mixture of ozone and peroxide and the titration carried out after the lapse of a few minutes, the number of c.c. of permanganate used (10.5 c.c.) was still less than had been the case in the previous experiment.

Another method had therefore to be devised to show that the reaction really took place without a catalytic agent. A current of ozone (free from nitrogen and oxides of nitrogen) was passed through a solution of hydrogen peroxide and the amount of unchanged peroxide was estimated, as before, after definite intervals of time. The concentration of the peroxide chosen was so great that the greatest possible concentration of ozone would not be nearly sufficient to destroy the peroxide originally taken, so that the catalytic effect during titration would necessitate only a small correction. In this way, it was found that the titre of the peroxide diminished from 14.8 to 1.6 in 205 minutes, whereas a similar current of oxygen merely caused this value to diminish from 24.0 to 23.6 in 410 minutes. This result shows that the original experimenters were correct, and that ozone does act slowly on hydrogen peroxide.

In conclusion, I wish to express my thanks to Sir W. Ramsay for the kind interest he has taken in the above experiments and for the advice and help he has given me.

## XCIX.—Some Physical and Chemical Properties of Strong Nitric Acid.

By VICTOR HERBERT VELEY and JOHN JOB MANLEY.

IN a recently published communication (this vol., p. 658), by W. N. Hartley, on the "Absorption spectra of nitric acid in various states of concentration," this author deals with certain physical and chemical properties of the concentrated acid, and partly confirms our earlier investigations bearing on this subject.

Moreover, since our more recent publications on the physical properties of nitric acid (*Proc. Roy. Soc.*, 1901, 69, 86, and *Phil Mag.*, 1902 [vi], 3, 118), an important investigation by R. Knietzsch (*Ber.*, 1901, 34, 4069) has appeared on the production of sulphur trioxide from flue gases, in which attention is drawn to the very remarkable alteration in physical and chemical properties of sulphuric acid containing 97—98 per cent.  $\text{H}_2\text{SO}_4$ . In the present communication, it is our desire to place on record, with reference to Hartley's communication, certain observations on nitric acid having a concentration of from 78 to 100 per cent.  $\text{HNO}_3$ , and to call attention to the close parallelism between nitric and sulphuric acids between the limits of 94 to 100 per cent. Hartley assumes the existence of orthonitric acid,  $\text{H}_3\text{NO}_4$ , from the observations of W. H. Perkin, senr., Pickering, ourselves, and others, and regards the anhydrous acid as having probably a bimolecular structure,  $\text{H}_2\text{N}_2\text{O}_6$ ; acids of concentration between 78 and 100 per cent. are considered to be mixtures of these two compounds, the former of which is an active agent, whilst the latter is inert.

So far as we are aware, the molecular weight of the anhydrous acid has not been determined or inferred either from the cryoscopic method or from investigations on the capillarity or dielectric constants, although the tendency of hydroxyl compounds to exist in some polymeric state supports Hartley's view.

Knietzsch apparently regards sulphuric acid containing 96 per cent.  $\text{H}_2\text{SO}_4$  as forming a kind of eutectic solution, but in the case of nitric acid of similar concentration we have considered the possibility of an initial formation of the compound  $2\text{HNO}_3, \text{N}_2\text{O}_5$ ; unfortunately, the properties of nitric acid containing nitric anhydride in solution have not been investigated, doubtless owing to experimental difficulties.

As the methods which we adopted for the measurement of the several physical constants have been fully described in our previous publications, we only bring forward our unrecorded results.



*Densities.*

In the following table, the values are given for the densities (reduced to a vacuum) of nitric acid from 78 to 100 per cent. concentration at  $4^{\circ}/4^{\circ}$ ,  $14\cdot2^{\circ}/4^{\circ}$ , and  $24\cdot2^{\circ}/4^{\circ}$  respectively. Confirmatory determinations made at different times, and with different instruments, are omitted:

TABLE I.

| Percentages. | Specific gravities.     |                                |                                |
|--------------|-------------------------|--------------------------------|--------------------------------|
|              | $4^{\circ}/4^{\circ}$ . | $14\cdot2^{\circ}/4^{\circ}$ . | $24\cdot2^{\circ}/4^{\circ}$ . |
| 78·22        | 1·47129                 | 1·45504                        | 1·43964                        |
| 79·14        | —                       | 1·46011                        | 1·44372                        |
| 79·59        | 1·47496                 | —                              | —                              |
| 81·97        | 1·48391                 | 1·46680                        | 1·45092                        |
| 84·90        | 1·49495                 | —                              | —                              |
| 85·21        | 1·49581                 | —                              | —                              |
| 85·80        | —                       | 1·47826                        | 1·46224                        |
| 87·55        | 1·50211                 | —                              | —                              |
| 87·90        | —                       | 1·48491                        | 1·46891                        |
| 89·73        | 1·50898                 | 1·49125                        | —                              |
| 92·34        | 1·51804                 | 1·49968                        | 1·48264                        |
| 94·04        | 1·51949                 | 1·50149                        | 1·48516                        |
| 95·62        | 1·52192                 | 1·50358                        | 1·48677                        |
| 96·64        | 1·52510                 | 1·50632                        | 1·48887                        |
| 97·33        | —                       | 1·50911                        | 1·49137                        |
| 98·07        | 1·53212                 | 1·51298                        | 1·49543                        |
| 99·97        | 1·54212                 | 1·52236                        | 1·50394                        |

If the densities are plotted as ordinates and the percentages as abscissæ, the values from 78 to 92 per cent. are on a straight line (within the limits due to analytical errors), and the value for 100 per cent. is situated on the same straight line produced, but the values from 92 to 100 per cent. lie on a curve below the straight line, the point of greatest concavity being at 96 per cent. approximately.

This phenomenon, although not strictly comparable, is analogous to that observed for sulphuric acid by Pickering, Knietzsch, and others, in that in the former case the densities increase continuously but slightly, whilst in the latter these increase up to 96—97 per cent. and then decrease.

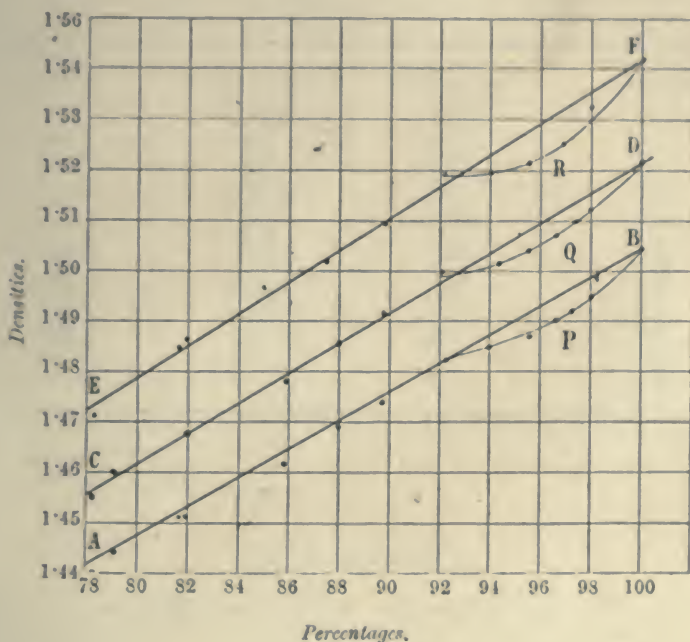
In Curve I (p. 1017), the values for  $24\cdot2^{\circ}/4^{\circ}$  are given along *APB*, for  $14\cdot2^{\circ}/4^{\circ}$  along *CQD* and  $4^{\circ}/4^{\circ}$  along *ERF* respectively.

*Contractions.*

If the contractions are deduced from the densities and calculated from an equation

$$C_1 = C - a(\Delta p) \dots\dots\dots (1)$$

wherein  $C_1$  is the contraction to be calculated,  $C$  the contraction at the selected origin of coordinates, in these cases at 77.7 or 78.0 per cent. ( $\text{H}_3\text{NO}_4 = 78.02$  per cent.  $\text{HNO}_3$ ),  $\alpha$ , a constant, and  $\Delta p$ , difference of percentage, then, as shown in the three succeeding tables, the



CURVE I.

values for  $C \times 10^{-5}$  from 78 to 92 per cent. are in accordance with those deduced from such an equation, within the limits of analytical errors. But from 92 to 100 per cent. the divergence is considerable and the maximum difference occurs at or about 96 per cent.

TABLE II.

*Contractions at 4°.**C* at 77.7 per cent. = 4660, *a* = -205.

| Percentages. | Values found. | Values calculated. | Difference. |
|--------------|---------------|--------------------|-------------|
| 78.22        | 4528          | 4554               | -26         |
| 79.59        | 4216          | 4272               | -56         |
| 81.93        | 3803          | 3799               | +4          |
| 85.21        | 3063          | 3120               | -53         |
| 87.55        | 2642          | 2641               | +1          |
| 89.73        | 2179          | 2193               | -14         |
| 92.34        | 1658          | 1658               | nil         |
| 94.04        | 1122          | 1310               | -88         |
| 95.62        | 672           | 986                | -314        |
| 96.64        | 438           | 777                | -339        |
| 98.07        | 252           | 482                | -232        |
| 99.97        | 8             | 8                  | nil         |

TABLE III.

*Contractions at 14.2°.**C* at 78 per cent. = 4590, *a* = -208.

| Percentages. | Values found. | Values calculated. | Difference. |
|--------------|---------------|--------------------|-------------|
| 78.22        | 4553          | 4545               | +8          |
| 79.14        | 4351          | 4353               | -2          |
| 81.97        | 3709          | 3764               | +55         |
| 85.86        | 2917          | 2969               | -42         |
| 87.90        | 2500          | 2531               | -31         |
| 89.73        | 2154          | 2150               | +4          |
| 92.34        | 1626          | 1607               | +19         |
| 94.04        | 1130          | 1255               | -125        |
| 95.62        | 672           | 925                | -253        |
| 96.67        | 448           | 713                | -265        |
| 97.33        | 333           | 571                | -238        |
| 98.07        | 247           | 415                | -168        |
| 99.97        | 8             | 8                  | nil         |



TABLE IV.

*Contractions at 24.2°.**C at 77.7 per cent. = 4623,  $\alpha = -195$ .*

| Percentages. | Values found. | Values calculated. | Difference. |
|--------------|---------------|--------------------|-------------|
| 78.22        | 4503          | 4522               | - 19        |
| 79.14        | 4391          | 4339               | + 52        |
| 81.93        | 3797          | 3795               | + 2         |
| 85.80        | 3024          | 3040               | - 16        |
| 87.90        | 2633          | 2631               | + 2         |
| 92.34        | 1770          | 1766               | + 4         |
| 94.04        | 1314          | 1433               | - 119       |
| 95.62        | 849           | 1126               | - 277       |
| 96.64        | 596           | 927                | - 331       |
| 97.33        | 486           | 793                | - 307       |
| 98.07        | 419           | 648                | - 229       |
| 99.97        | 6             | 6                  | nil         |

Owing to the great differences in the values for the contractions, it is not convenient to illustrate the foregoing results by curves drawn on a sufficiently small scale.

*Electrical Conductivity.*

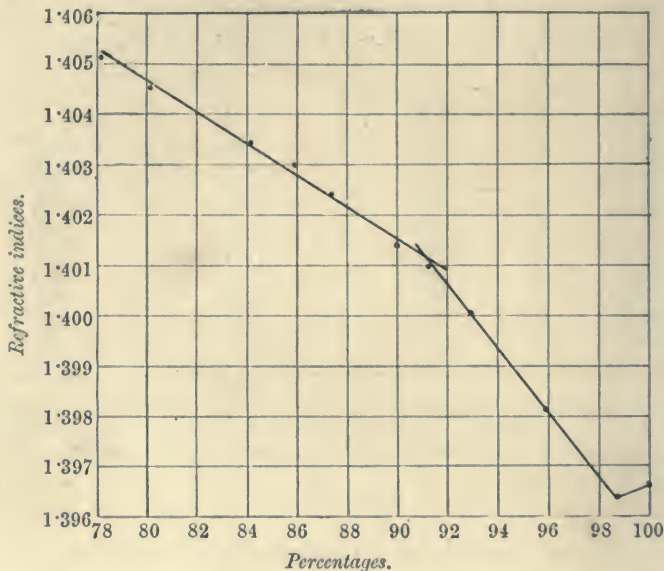
We have previously shown that nitric acid of about 96 per cent. concentration shows a minimum conductivity, and, moreover, at concentrations above 94 per cent. it behaves as a metallic, and not as an electrolytic, conductor in possessing negative temperature coefficients. As regards the former point, the observations of Knietzsch in the case of sulphuric acid are precisely analogous, but he does not appear to have studied the temperature coefficients of sulphuric acid either immediately below or above the limit of the anhydrous acid,  $\text{H}_2\text{SO}_4$ .

*Refractive Indices.*

If a curve is drawn having for coordinates the refractive indices ( $\mu_{\text{D}_{14}}$ ) of nitric acid and the corresponding percentage compositions, the points which indicate concentrations of from 78 to 91 per cent. lie on a straight line, but the values from 91 to 98 per cent. are situated on another straight line, then from 98 to 100 per cent. there is a slight reversal, as in the case of the electrical conductivities (see Curve II, p. 1020). At present, the only observations on the refractive indices of concentrated sulphuric acid are those by van der Willigen (*Archives Musée Teyler*, 1868, 1, 74), which are not carried beyond a con-

centration of 94.7 per cent. (approximately). We hope shortly to carry out an investigation on this subject.

It would thus appear from the above considerations that nitric acid containing about 96 per cent. anhydrous acid, like sulphuric acid of a similar concentration, forms a kind of eutectic solution (compare



CURVE II.

Knietzsch, *ibid.*), and adopting Hartley's hypothesis of an admixture or combination of orthonitric and nitric acids, such an acid would probably have the composition  $3\text{H}_2\text{N}_2\text{O}_6, \text{H}_3\text{NO}_4$  (95.9 per cent.  $\text{HNO}_3$ ). Determinations of the physical constants of nitric acid containing nitric anhydride in solution might throw further light on this point.

#### *Chemical Properties.*

It is a further point of interest to ascertain if there are certain substances on which nitric acid of the above-mentioned critical concentration is less reactive than more or less concentrated acids, just as the analogous sulphuric acid is less reactive on iron and steel. We understand that Hartley proposes to study the chemical properties of concentrated nitric acid more fully and precisely, with the view of ascertaining its constitution. To our previous observations on this subject, we now add the following: Nitric acid of approximately 100 per cent. concentration nitrated cotton directly without addition of sulphuric acid, and so far as qualitative experiments went, it appeared that cotton thus directly nitrated was as inflammable as ordinary gun-cotton. Difficulties were experienced in estimating the

proportion of nitrous acid (or nitrogen peroxide) by means of the *m*-phenylenediamine reaction, doubtless owing to some secondary reaction.

### *Summary.*

Nitric acid of 96 per cent. and sulphuric acid of 98 per cent. concentration show definitely marked characteristics, analogous, although not in all cases strictly parallel, as regards certain properties, more especially density, contraction, and electrical conductivity; also in the case of the former, refractive indices, as investigated by ourselves, and in the case of the latter chemical reactivity, boiling point, vapour pressure, and, to a less degree, viscosity and capillarity, as investigated by Knietzsch.

The precise constitution of acids having these critical concentrations remains at present a matter for further inquiry.

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## C.—*The Alkylation of Sugars.*

By THOMAS PURDIE, F.R.S., and JAMES C. IRVINE, Ph.D., D.Sc.

IN the course of the earlier researches on the synthesis of glucosides, attempts were no doubt frequently made to prepare alkyl ethers of the sugars. Berthelot (*Ann. Chim. Phys.*, 1860, [iii], 60, 103), by heating cane sugar with caustic potash and ethyl bromide, obtained a substance which he describes as a diethylglucosan ether. Practically, however, the only methods of alkylating sugars at present known are those of Fischer (*Ber.*, 1893, 26, 2400; 1895, 28, 1145) and of Koenigs and Knorr (*Ber.*, 1901, 34, 957); in the former process, the alkylation is effected by the direct action of alcohol on the sugar in the presence of hydrochloric acid, whilst the latter is due to the interaction of alcohol and the acetohalogen or acetonitro-derivative, and subsequent removal of the acetyl groups by hydrolysis with alkali. By these methods, as is well known, only one of the carbinol groups of the sugar is etherified, and the products are of a glucosidic nature. Alkyl ethers of the sugars in the stricter sense of the term, that is to say, ethers which retain the aldehydic or ketonic properties of the parent sugar and resist the action of hydrolysing agents, are, however, so far unknown. The main purpose of the following research was the preparation and investigation of compounds of this class.

In alkylating the esters of optically active hydroxy-acids, we found that the object could be attained, when other methods had failed, as in the case of malic, lactic, and tartaric esters (*Trans.*, 1899, 75, 153, 483; 1901, 79, 957) and of mandelic esters (McKenzie, *Trans.*, 1899, 75, 753),





Trans., 1901, 79, 668) can be etherified, the latter almost quantitatively, by means of silver oxide and alkyl iodide, the method proved inapplicable to the reducing sugars. When silver oxide was added to a mixture of glucose, dissolved in methyl alcohol and methyl iodide, a vigorous reaction ensued, and when a large excess of the alkylating agent was used a product soluble in ether but having an acid reaction was obtained. On attempting to distil this, much decomposition occurred, and the only substance isolated was methyl oxalate. When ethyl iodide was employed in a similar reaction, the product was also acid, and an analysis of the silver residues showed that only 45 per cent. of the silver oxide taken was converted into iodide, the remainder having been reduced to the metallic state. The reaction was evidently a complex one. An attempt to alkylate *lævulose* by this method was also unsuccessful.

To avoid oxidation, it was evidently requisite that the aldehydic or ketonic group of the sugar should be masked, and instead of glucose, therefore, we used Fischer's easily accessible  $\alpha$ -methylglucoside. Methyl iodide was employed throughout our experiments, as previous experience with tartaric esters had shown that the slower action of the higher iodides gave scope for the occurrence of oxidation which resulted in the production of oxalates in considerable quantity.

The methylglucoside in methyl alcoholic solution reacted readily with methyl iodide in the presence of silver oxide, and was found to be nearly proof against the oxidising action of the latter. The product, consisting of a mixture of methyl ethers of the glucoside, was a neutral, viscid syrup, soluble in ether, having no action on Fehling's solution and distilling without decomposition in a vacuum. The solubility in organic solvents and the volatility of these compounds, as was to be expected, increase with the number of the methoxyl groups present in the molecule, and it was found possible, therefore, to isolate the main constituent of the mixture by fractional distillation. This substance, which proved to be a trimethyl methylglucoside, boils at 167—170° under 17 mm. pressure and is readily hydrolysed by dilute hydrochloric acid, giving a syrup which reduces Fehling's solution vigorously. It is shown in the succeeding paper that three of the four methoxyl groups are retained throughout the hydrolysis, the product being a trimethyl glucose. Attempts to obtain a hydrazone or osazone from this compound having failed, evidence of its aldose nature was sought by oxidising it with bromine water according to Kiliani's method. The process gave an almost neutral syrup, an analysis of which after distillation gave figures approximating to those for trimethylgluconolactone. The lactonic nature of the compound was confirmed by titration with alkali and by the gradual change in the optical rotation of its solution.

As stated above, the main product of the methylation when it is



carried out in methyl alcohol is a trimethyl methylglucoside. The last remaining hydroxyl, probably that of the terminal primary carbinol group of the chain, alkylates more slowly than the others. Even when the alkylating agent was used in considerable excess, the tetramethyl derivative was produced in very small quantity. This is partly due to the fact, which is evident from the abundant production of dimethyl ether in the course of the process, that the alkylation extends to the solvent alcohol, and that much of the alkylating agent is thus lost. Complete alkylation of the glucoside can, however, be effected by taking advantage of the fact that the trimethyl methylglucoside is readily soluble in methyl iodide. Such a solution reacts readily with silver oxide, and under these conditions tetramethyl methylglucoside is obtained as a neutral, comparatively mobile liquid boiling at 144—145° under 17 mm. pressure and showing no action on Fehling's solution.

On hydrolysing this compound with dilute hydrochloric acid, the glucosidic methoxyl only is removed, and a tetramethylated glucose is produced, which distils without decomposition at 182—185° under 20 mm. pressure and gradually solidifies; by recrystallising from warm ligroin, it is obtained in long needles melting at 81—83°. The compound reduces both Fehling's solution and ammoniacal silver nitrate on warming, and has undoubtedly the structure of an aldose. To indicate this and to distinguish it from the isomeric trimethyl methylglucoside referred to above, it may be named tetramethyl glucose.

Although the substance reacted with phenylhydrazine, attempts to procure from it an osazone or crystallised hydrazone were not successful, but evidence of its nature was procured, as before, by Kiliiani's process of oxidising aldoses to aldonic acids. The product was an acid oil, soluble in ether, but dissolving completely in water only on heating. Analysis of the substance dried at 100° in a vacuum showed it to be tetramethyl gluconolactone. This conclusion was confirmed by the analysis of a barium salt prepared from it, also by its behaviour on neutralisation, and by the gradual diminution in specific rotation shown by its aqueous alcoholic solution.

Tetramethyl glucose was obtained, as stated, by hydrolysing tetramethyl  $\alpha$ -methylglucoside. With the idea of ascertaining whether the methyl group lost in hydrolysis could be re-introduced by our method of alkylation, and, if so, whether this would result in the reproduction of the initial compound or an isomeride, the crystalline tetramethyl glucose was dissolved in methyl iodide and treated with silver oxide.

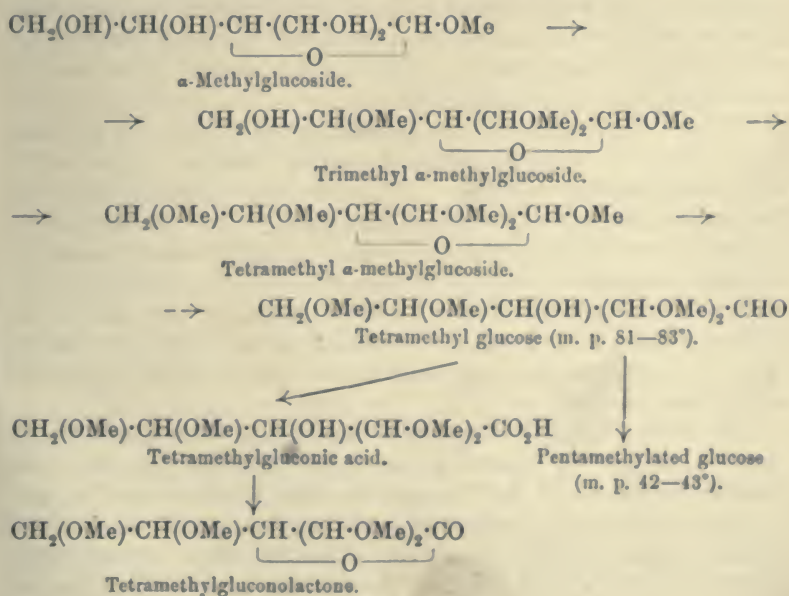
The product was a neutral oil distilling without decomposition at 124—127° under 8 mm. pressure, which, after 3 months, deposited crystals melting at 42—43°. Analysis of the crystalline substance showed it to be a pentamethylated glucose; it reduced ammoniacal



silver nitrate, but did not reduce Fehling's solution even on boiling. That the substance is, however, isomeric and not identical with tetramethyl  $\alpha$ -methylglucoside is proved by its crystalline character, its lower boiling point, and its different optical activity. Of the three pentamethyl glucoses alluded to in the introduction, it must be either tetramethyl  $\beta$ -methylglucoside or the pentamethyl glucose of aldehydic structure. As a test made with our first preparations showed no action on Fehling's solution after warming with dilute aqueous hydrochloric acid, we concluded that the substance was the latter compound. On repeating the experiment on a second preparation, however, reduction of this solution was observed. The amount of material at our disposal being too small for further investigation, the structure of the compound must remain in doubt for the present. Its levorotatory power favours the view that it is the  $\beta$ -glucoside.

Examination of the oil, which deposited the crystals just described, showed that it probably contained tetramethyl  $\alpha$ -methylglucoside. It reduced Fehling's solution only after being hydrolysed, and the product of hydrolysis yielded a minute quantity of crystals, which, from their melting point, seemed to be impure tetramethyl glucose. It appears, therefore, that by the methylation of this compound two of the three pentamethylated glucoses are produced.

Adopting Fischer's formula for methylglucoside and omitting the product of hydrolysis of the trimethyl derivative, the following scheme represents the relations of the compounds described:



With regard to the optical activity of the glucose derivatives described in this and the succeeding paper, all are dextrorotatory except the above-mentioned pentamethylated glucose, which is lævorotatory. The specific rotations recorded later were determined for the most part in dilute solution, and are therefore subject to considerable experimental error. It must also be stated that the results obtained in different preparations of the same substance were not concordant. The figures quoted below, however, suffice to show that it is the methyl group in the glucosidic position that chiefly affects the optical activity, the conversion of glucose into glucoside causing in each case a great increase in the dextrorotation, whilst the introduction of methyl groups to form true ethers, whether in the glucose or the glucoside, produces a much less marked effect.

|                              | Solvent.                        | $[\alpha]_D$ . |
|------------------------------|---------------------------------|----------------|
| Glucose.....                 | H <sub>2</sub> O                | + 52·6°        |
| Trimethyl glucose .....      | CH <sub>4</sub> O               | 79·2           |
| Tetramethyl glucose .....    | C <sub>2</sub> H <sub>6</sub> O | 78·2           |
| Methylglucoside .....        | H <sub>2</sub> O                | 157·5          |
| Trimethyl methylglucoside... | C <sub>2</sub> H <sub>6</sub> O | 150·2          |
| Tetramethyl methylglucoside  | C <sub>2</sub> H <sub>6</sub> O | 140·5          |

The discordant observations of optical activity, exhibited more particularly in different preparations of tri- and tetra-methyl  $\alpha$ -methylglucosides, may be accounted for by the presence of impurities, as the fractionation of such viscid liquids was necessarily attended with much difficulty; or they may be due to partial conversion of the compounds into isomerides by intramolecular rearrangement during the repeated treatments with methyl iodide. The activity of these two substances was not impaired by redistillation.

We have formulated the tri- and tetra-methyl glucoses on the basis of the aldehydic formula commonly used for the parent sugar. It is, of course, probable that these compounds are subject to tautomeric change like glucose itself, although it is worthy of note in this connection that we obtained no distinct evidence of multirotation in the case of either compound. We hope to make a thorough examination of the crystalline tetramethyl glucose from this point of view, and in particular to ascertain whether, on hydrolysis, tetramethyl  $\beta$ -methylglucoside yields the same compound as the corresponding  $\alpha$ -glucoside or a stereoisomeride.

Our results supply evidence of some interest in support of the formula adopted by Fischer for his alkylglucosides (*loc. cit.*). The general correctness of this formula has been amply verified by subsequent research, but positive evidence with respect to the position of the oxygen coupling of the ring is still lacking. Fischer's view that the oxygen is linked to the  $\gamma$ -carbon atom is mainly based on the



fact that benzoylcarbinol, benzoin, and glycolaldehyde (*Ber.*, 1897, 30, 3055) do not yield derivatives of a glucosidic nature, and that the group  $\text{CO}\cdot\text{CH}\cdot\text{OH}$ , therefore, does not suffice for the formation of glucosides. The alternative linkage, that of the ethylene oxide type, was supported by Marchlewski, and his arguments in favour of this formula were replied to by Fischer. Lobry de Bruyn and Ekenstein, however (*Ber.*, 1895, 28, 3078), consider that the interconversion of glucose, levulose, and mannose by the action of alkalis lends support to Marchlewski's view. The fact that our tetramethylgluconic acid forms a lactone shows that its one unmethylated carbinol group is that in the  $\gamma$ -position; it follows, necessarily, that in the tetramethyl methyl glucoside from which the acid was derived, and, consequently, also in the parent methylglucoside, it is the  $\gamma$ -carbon atom which is united with the oxygen of the ring. Fischer's formula is thus confirmed.

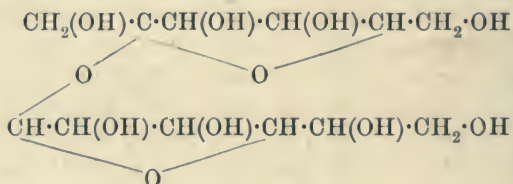
Preliminary experiments show that methylfructoside behaves like the corresponding glucoside, and yields, when completely methylated, tetramethyl methylfructoside, a syrup boiling without decomposition at  $132\text{--}136^\circ$  under 10 mm. pressure. The method of alkylation has also been applied satisfactorily to acetone rhamnoside. According to Fischer's formula (*Ber.*, 1895, 28, 1150), the substance contains two unetherified secondary carbinol groups. By carrying out the alkylation first in acetone and then in methyl iodide solution, the hydroxyl of both groups is methylated with the production of dimethyl acetone rhamnoside. The substance is an oil of pleasant odour, distilling readily at  $115\text{--}118^\circ$  under 11 mm. pressure. The introduction of the methyl groups changes the sign of rotation, the compound being lævorotatory. A detailed description of the results obtained with the fructoside and rhamnoside will be given in a later communication.

Our method of alkylation can also be applied to bioses. In the case of maltose, as was to be expected, the reaction is complicated by the occurrence of oxidation, and we have not been able as yet to isolate any of the products in a pure state. Cane sugar, however, gives results of some interest. It was to be expected that this sugar, owing to the absence of free aldehydic groups in its composition, would lend itself readily to the reaction; on the other hand, the very slight solubility of the substance in all solvents in which the process can be carried out seemed an insurmountable difficulty. The solubility of a sugar in organic solvents, however, increases as the methylation proceeds, and we found, accordingly, that by repeated alkylations, first in aqueous methyl alcohol and then in dry alcohol, a syrup entirely soluble in methyl iodide was produced, and the methylation was therefore completed in the latter solvent. In this manner, a neutral oil was finally obtained which showed no action on Fehling's solution until it was hydrolysed. The product of hydrolysis was a



viscid liquid which, after a time, partly crystallised. The crystalline substance, when purified by recrystallisation from ligroin, was recognised by its melting point and by analysis to be identical with the tetramethyl glucose previously prepared from glucose. The uncrystallisable portion of the oil no doubt contains the corresponding derivative of lævulose, which may possibly be isolated by distillation or otherwise.

Fischer (*Ber.*, 1893, 26, 2404), after developing the constitution of the alkylglucosides, concludes that the complex carbohydrates probably possess a similar structure. Modifying the formula suggested by Tollens (*Ber.*, 1883, 16, 923), he accordingly represents the constitution of cane sugar as follows:



and Perkin has recently shown (*Trans.*, 1902, 81, 185) that this view is corroborated by the magnetic rotation of the sugar.

The fact, just mentioned, that methylated cane sugar and methylated methylglucoside give, on hydrolysis, the same tetramethyl glucose, proves that the constitution and linkage of the glucose group of the biose is the same as that of the simple glucoside. This, coupled with the evidence given above of the constitution of tetramethyl glucose, furnishes conclusive evidence, at least so far as the glucose half of the molecule is concerned, of the correctness of Fischer's formula.

#### *Trimethyl α-Methylglucoside.*

The α-methylglucoside used was prepared by Fischer's method (*loc. cit.*), the yield of product obtained (m. p. 165—167°) being 73 per cent. of the weight of glucose used.

The method of alkylation finally adopted was as follows: the dry silver oxide (5 mols.) was added to the mixture of methyl iodide (10 mols.) and methylglucoside (1 mol.) dissolved in six to seven times its weight of pure methyl alcohol. The methyl iodide was kept in excess of the oxide during the process, and to obviate precipitation of the glucoside it was added in several instalments, each addition being followed by the corresponding amount of the oxide. The action, which was started after each addition by slightly warming the mixture, was then allowed to proceed spontaneously, and finally completed by heating for some time on a water-bath under a reflux condenser.

The silver residues having been filtered off and washed with hot methyl alcohol, the filtrate was evaporated to dryness, and the residual syrup was then extracted with ether, the alkylated products being thus removed and any unaltered glucoside precipitated. The ethereal extract, dried with anhydrous sodium sulphate and then evaporated, left a viscid syrup, which was distilled on a graphite bath under reduced pressure. The total distillate, boiling at 157—165° under 14 mm. pressure, amounted to about half the weight of glucoside taken. After several fractional distillations, a liquid boiling at 167—170° under 17 mm. pressure was collected, which was analysed with the following results:

0.1999 gave 0.3723 CO<sub>2</sub> and 0.1506 H<sub>2</sub>O. C=50.79; H=8.37.

C<sub>10</sub>H<sub>20</sub>O<sub>6</sub> requires C=50.85; H=8.47 per cent.

That the substance was not merely a mixture of different alkylated products is proved by the fact that the same liquid of constant boiling point was obtained in other experiments when different proportions of the alkylating agent were used, and even when the glucoside employed was a crude, syrupy mixture of the  $\alpha$ - and  $\beta$ -forms. In the latter preparation, a better method of isolating the product was apparently employed, because combustions of successive distillations gave the following results:

I. C=50.84; H=8.61. II. C=50.87; H=8.58.

As the various methylated derivatives do not differ very much in elementary composition, the methoxyl was determined by Zeisel's method:

0.4704 gave 1.7864 AgI. CH<sub>3</sub>O=50.13.

0.3292 „ 1.2480 AgI. CH<sub>3</sub>O=50.04.\*

C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub> requires CH<sub>3</sub>O=52.54 per cent.

A determination of the molecular weight of the substance by the cryoscopic method in aqueous solution gave 209, the calculated value being 236. The substance is therefore trimethyl  $\alpha$ -methylglucoside. When warmed, it is a colourless, fairly mobile liquid, but on cooling it becomes a viscid syrup, which, after the lapse of a year, shows no sign of crystallising. The substance has a slightly sweet taste; it is soluble in water, alcohol, and ether, and has no action on Fehling's solution.

Observations of the specific rotation in alcoholic solution gave:  $l=1$ ,  $c=15.86$ ,  $\alpha_D^{20}+19.96^\circ$ , hence  $[\alpha]_D^{20}$  is  $+125.9^\circ$ ; a solution obtained by diluting 5 c.c. of this to 15 c.c. gave  $[\alpha]_D^{20}+126.8^\circ$ .† An

\* The quantity of substance used in these determinations was too large. A better result is recorded in the succeeding paper.

† An observation showing a much higher specific rotation is recorded in the succeeding paper.

observation of the specific rotation of the pure liquid, made at  $30^\circ$  so as to admit of the substance being manipulated, gave:  $d_{30^\circ/4^\circ} = 1.1656$ ,  $\alpha_D^{30^\circ} + 75.66^\circ$ ;  $l = 0.5$ ;  $[\alpha]_D^{30^\circ} + 129.8^\circ$ .

When the alkylating agent is used in the proportion given above, little or no unchanged glucoside is left, and the undistilled residues and less volatile fractions consist of mono- and di-methylated derivatives, the percentage of carbon in which is raised by repeated alkylation. When a larger proportion of alkylating agent is used, the more volatile tetramethyl ether is produced in small quantity. It was, however, extremely difficult, even by repeated alkylation, to extend the process beyond the trimethyl stage so long as any methyl alcohol was present. The further examination of this compound is described in the succeeding paper.

#### *Tetramethyl $\alpha$ -Methylglucoside.*

On alkylating again some of the lower methylated ethers from the previous experiments without the use of other solvent than methyl iodide, we found that the final distilled product, which was comparatively mobile, had a much lower boiling point than the trimethyl ether, and its composition approximated to that of a tetramethyl methylglucoside. The same process was therefore applied to the pure trimethyl ether, the following experiment being quoted as an example of the method employed. A very large excess of alkylating agent was used, the quantities taken being 15 grams of trimethyl ether (1 mol. reckoned as methylglucoside), 115 grams of methyl iodide (10 mols.), and 90 grams of dry silver oxide (5 mols.). The ether was dissolved in half the total amount of iodide, and then half the oxide was added in small quantities, the mixture being heated after each addition. The action was feeble, and when the rest of the alkylating material had been similarly added the mixture was heated for some hours on a water-bath. The liquid obtained after filtering and extracting the silver residues with ether was dried with anhydrous sodium sulphate and evaporated. On distilling the residual neutral oil, 10 grams were collected which boiled at  $144\text{--}152^\circ$  under about 20 mm. pressure, and fractionation yielded 6.2 grams boiling steadily at  $144\text{--}145^\circ$  under 17 mm. pressure. The results of analysis and of the methoxyl determination in two different preparations were as follows:

0.1794 gave 0.3480  $\text{CO}_2$  and 0.1426  $\text{H}_2\text{O}$ . C = 52.90; H = 8.83.

0.2144 „ 0.4134  $\text{CO}_2$  „ 0.1673  $\text{H}_2\text{O}$ . C = 52.59; H = 8.67.

0.1378 „ 0.6484 AgI.  $\text{CH}_3\text{O} = 62.11$ .

0.1822 „ 0.8494 AgI.  $\text{CH}_3\text{O} = 61.54$ .

$\text{C}_{11}\text{H}_{22}\text{O}_6$  requires C = 52.80; H = 8.80.  $\text{C}_6\text{H}_7\text{O}(\text{OCH}_3)_5$  requires  $\text{CH}_3\text{O} = 62.0$ .



Analysis of a third preparation gave C = 52.45; H = 8.86;  $\text{CH}_3\text{O}$  = 61.04 per cent.

In preparing this compound, it is unnecessary to isolate the trimethyl ether. The crude syrup containing the latter, obtained from the alkylation in methyl alcohol solution, may be alkylated after drying by heating in a vacuum in methyl iodide solution in the manner described above. If the less volatile fractions are again alkylated, the yield is about 55 per cent. of the glucoside taken.

Tetramethyl  $\alpha$ -methylglucoside is a colourless, neutral, syrupy liquid possessing a burning taste; it is soluble in water, alcohol, acetone, ether, and methyl iodide, and has no action on Fehling's solution. Determinations of the specific rotation made on different preparations gave discordant results, as mentioned in the introduction. The following observations were made in a 2 dm. tube:

|                            | $c$ .  | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . |
|----------------------------|--------|-------------------------|---------------------------|
| I. In ethyl alcohol.....   | 5.4233 | +13.86°                 | +127.8°                   |
| II.     "     "     "..... | 5.0090 | 14.08                   | 140.5                     |
| Water.....                 | 5.005  | 13.63                   | 136.2                     |

The solutions did not exhibit multirotation, and the optical activity was but slightly altered by redistilling the substance.

The specific rotations of the two preparations in the form of pure liquids were:

- I.  $l = 0.5$ ,  $\alpha_D^{20^\circ} + 70.5^\circ$ ;  $d \ 20^\circ/4^\circ = 1.1006$ ,  $[\alpha]_D^{20^\circ} + 128.1^\circ$ .  
 II.  $l = 0.5$ ,  $\alpha_D^{20^\circ} + 77.5^\circ$ ;  $d \ 20^\circ/4^\circ = 1.1025$ ,  $[\alpha]_D^{20^\circ} + 140.6^\circ$ .

The specific rotation of the liquid substance is nearly the same as in alcoholic solution; in aqueous solution, it is considerably lower.

### *Tetramethyl Glucose.*

To prepare this substance, tetramethyl  $\alpha$ -methylglucoside is boiled with 8 per cent. aqueous hydrochloric acid for half an hour and the dark coloured solution is then neutralised with sodium hydroxide and evaporated. As evaporation proceeds, a part of the product of hydrolysis separates as an oil and must be removed by extraction with ether. The residue left on complete evaporation is boiled with alcohol and, sodium chloride having been filtered off, the alcoholic liquid is evaporated. The residual syrup is then extracted with boiling ether, which leaves the greater portion of the colouring matter undissolved; the ethereal solution, to which is added the solution containing the above-mentioned oil, after being decolorised with animal charcoal and dried with sodium sulphate, is completely evaporated. The residue is a pale yellow oil consisting mainly of tetramethyl

glucose and unaltered tetramethyl methylglucoside. To separate these, the mixture may be extracted with boiling ligroin, which dissolves the former, or it may be distilled. In the latter case, the unaltered glucoside ether passes over first, after which the thermometer rises quickly, when the tetramethyl glucose is collected as a viscous liquid boiling at 182—185° under 20 mm. pressure and slowly crystallising in long needles. This less volatile distillate contains, however, a considerable quantity of uncrystallisable oil, from which the crystals have to be separated by means of a porous tile. A further quantity of substance is obtained by extracting the tile with ether, evaporating, and extracting the residual syrup with boiling ligroin. When recrystallised from this liquid, it is deposited in beautiful tufts of radiating needles melting at 81—83°. The yield of the recrystallised compound was 35 per cent. of the weight of tetramethyl methylglucoside taken.

The analysis of two different preparations and a methoxyl determination were made with the following results :

- I. 0.1705 gave 0.3165 CO<sub>2</sub> and 0.1344 H<sub>2</sub>O. C = 50.63 ; H = 8.69.  
 0.1537 „ 0.6137 AgI. CH<sub>3</sub>O = 52.70.  
 II. 0.1933 „ 0.3578 CO<sub>2</sub> and 0.1460 H<sub>2</sub>O. C = 50.48 ; H = 8.39.  
 0.1612 „ 0.3010 CO<sub>3</sub> „ 0.1250 H<sub>2</sub>O. C = 50.92 ; H = 8.62.  
 C<sub>10</sub>H<sub>20</sub>O<sub>6</sub> requires C = 50.85 ; H = 8.47. C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub> requires  
 CH<sub>3</sub>O = 52.54 per cent.

The substance has a bitter taste and is neutral to litmus ; it is readily soluble in all ordinary organic solvents, but sparingly so in ligroin. Fehling's solution is reduced on boiling, and ammoniacal silver nitrate on gently warming. The aqueous solution becomes yellow and finally brown on boiling with dilute alkali, and with  $\alpha$ -naphthol and concentrated sulphuric acid (Molisch reaction) the substance behaves like glucose.

Observations of the specific rotation gave the following results :

In alcohol :  $l = 2$ ,  $c = 5.0083$ ,  $\alpha_D^{20} + 7.83^\circ$ , hence  $[\alpha]_D^{20} 78.2^\circ$ .

In water :  $l = 2$ ,  $c = 5.0183$ ,  $\alpha_D^{20} + 8.11^\circ$ , hence  $[\alpha]_D^{20} 80.8^\circ$ .

After 24 hours, the observed rotation of this solution rose by 0.22°, the specific rotation thus becoming 83.0°; 24 hours later the reading appeared to be constant. The compound therefore exhibits the property of multirotation to a very slight extent, if at all.

Trimethyl glucose and phenylhydrazine readily interact in molecular proportions with the production of an oil insoluble in water, very soluble in alcohol, ether, and benzene. The substance could not be made to crystallise, but, as indicated below, it is doubtless a hydrazone.

When the pure base and the methylated sugar were mixed in ethereal solution in the proportion indicated, only a slight coloration ensued, which was not much increased when the solution was heated at 55° in a sealed tube. Reaction had, however, occurred, as the oil which was left on evaporating the ether, after having been washed with dilute acetic acid, had no action on Fehling's solution. When a dilute acetic acid solution of the base was added to the sugar derivative in the same proportions as before, the latter dissolved at once, and the solution subsequently deposited a light yellow oil. The interaction of the substance was evidently complete, as only a minute quantity of phenylhydrazine acetate was found in the aqueous layer. Although the oil, after having been washed with water, had no action whatsoever on Fehling's solution, even on boiling, yet that it nevertheless contained both the sugar and hydrazine residues was proved by the positive results obtained on applying the Zeisel test for methoxyl and the ordinary test for nitrogen. Attempts to recover the methylated glucose by decomposing the compound with benzaldehyde or with fuming hydrochloric acid were unsuccessful, but it behaved towards the latter reagent like a hydrazone, as the product of the action at once reduced Fehling's solution in the cold.

#### *Tetramethylgluconic Acid.*

Tetramethyl glucose is readily converted into this acid by the action of bromine water. The oxidation was carried out according to the method of Kiliani and Kleemann (*Ber.*, 1884, 17, 1298) for the preparation of gluconic acid, the quantities of material used being 4.3 grams of tetramethyl glucose, 10.6 grams of bromine, and 21.5 grams of water. The bromine was added gradually with frequent shaking, and after 15 hours the small quantity of this element left was boiled off; the hydrobromic acid was then removed with silver oxide and the dissolved silver by means of sulphuretted hydrogen. The residue left on evaporation was dissolved in ether in order to remove some barium salt formed from traces of barium carbonate contained in the silver oxide, and the ethereal solution, after being treated with anhydrous sodium sulphate, was evaporated to dryness. The residue was a pale yellow oil weighing 2.6 grams, which consisted mainly of tetramethylgluconolactone; it was prepared for analysis by heating at 100° under reduced pressure, but no further attempt was made to purify the substance.

The following analytical results were obtained with different preparations:

0.1771 gave 0.3288 CO<sub>2</sub> and 0.1228 H<sub>2</sub>O. C = 50.63; H = 7.70.

0.3156 „ 0.5946 CO<sub>2</sub> „ 0.2204 H<sub>2</sub>O. C = 51.38; H = 7.75.

C<sub>10</sub>H<sub>18</sub>O<sub>6</sub> requires C = 51.28; H = 7.69 per cent.



The result of a determination of methoxyl showed that these groups had not been affected by the oxidation :

0.1455 gave 0.5934 AgI.  $\text{CH}_3\text{O} = 53.83$ .

$\text{C}_6\text{H}_6\text{O}_2(\text{OCH}_3)_4$  requires 52.99 per cent.

The lactone, which was found to volatilise at  $100^\circ$  under reduced pressure, condensed as an oil ; it formed oily globules in water which disappeared on warming, and produced an acid solution. When treated with alkali, it showed the characteristic behaviour of a lactone. An alcoholic solution containing 0.2646 gram of the substance was titrated with an aqueous solution of barium hydroxide (1 c.c. = 0.01052), phenolphthalein being used as indicator. The pink colour produced on adding a small quantity of the alkali gradually disappeared, and the solution after some time was again distinctly acid. After adding 5 c.c., the colour was persistent for about a minute in the cold ; it finally remained quite permanent, even on boiling, after the addition of 9.50 c.c.  $\text{C}_{10}\text{H}_{18}\text{O}_6$ , calculated as lactone, requires 9.22 c.c. for neutralisation.

It was found impossible to isolate the acid or to obtain crystalline salts. The calcium salt is a gum, the cadmium salt a glass, and both are soluble in alcohol.

The barium salt was obtained for analysis by the following process : the solution prepared by digesting the aqueous solution of the lactone with barium carbonate was evaporated to dryness ; the residual glass was powdered, dried at  $110^\circ$ , treated with boiling ether to remove extraneous organic matter, and then taken up in alcohol. On the addition of ether to the solution thus obtained, the salt separated as a perfectly white, bulky, gelatinous precipitate, which was collected, washed with ether, and dried at  $115^\circ$  for analysis :

I. C = 37.69 ; H = 5.99 ; Ba = 21.46.

II. C = 37.49 ; H = 5.85 ; Ba = 21.50.

$\text{C}_{20}\text{H}_{38}\text{O}_{14}\text{Ba}$  requires C = 37.54 ; H = 5.94 ; Ba = 21.49 per cent.

The optical activity of the lactone was determined in an aqueous alcoholic solution containing 0.4837 gram in 20 c.c. The rotation observed immediately after the solution was prepared was  $+4.87^\circ$  in a 2 dm. tube ; this decreased in 1 hour 45 minutes to  $3.58^\circ$ , and after three days to  $1.91^\circ$ , the specific rotation having thus fallen from  $100.7^\circ$  to  $39.5^\circ$ .

#### *Methylation of Tetramethyl Glucose.*

In a preliminary attempt to methylate tetramethyl glucose with silver oxide and methyl iodide, a mobile oil was obtained which boiled considerably lower and showed on analysis a higher percentage of

carbon than the original substance; after three months, the liquid deposited slender prisms melting at  $39-40^{\circ}$ . The experiment was accordingly repeated, the material used being 2 grams of tetramethyl glucose, 20 grams of methyl iodide, and 12 grams of silver oxide. The substituted glucose dissolved easily in the iodide, and on adding the oxide a feeble although appreciable reaction ensued which was completed by heating for 6 hours on a water-bath under a reflux condenser. The ethereal solution of the product, after drying with sodium sulphate, was evaporated, and the residual oil was distilled; the total distillate between  $124^{\circ}$  and  $135^{\circ}$  under 8 mm. pressure weighed 1.7 grams, and of this, 1.09 grams were collected at  $124-127^{\circ}$ . The crystallisation of this fraction was induced at once by introducing a small fragment of the previously prepared substance. After being freed from the oil in which they were imbedded by drying on a porous tile, the crystals weighed 0.48 gram and melted at  $42-43^{\circ}$ . On account of the small quantity of available material, the substance had to be analysed without further purification:

0.1318 gave 0.2546  $\text{CO}_2$  and 0.1057  $\text{H}_2\text{O}$ .  $\text{C} = 52.68$ ;  $\text{H} = 8.91$ .

0.1464 „ 0.2835  $\text{CO}_2$  and 0.1178  $\text{H}_2\text{O}$ .  $\text{C} = 52.81$ ;  $\text{H} = 8.91$ .

0.1333 „ 0.6213  $\text{AgI}$ ;  $\text{CH}_3\text{O} = 61.52$ .

$\text{C}_6\text{H}_7\text{O}(\text{OCH}_3)_5$  requires  $\text{C} = 52.80$ ;  $\text{H} = 8.80$ ;  $\text{CH}_3\text{O} = 62.00$ .

The compound is therefore a pentamethylated glucose isomeric with the tetramethyl  $\alpha$ -methylglucoside already described; we are unable, however, at present to say whether it is the glucosidic or the aldehydic isomeride.

The substance became brown on boiling with alkali, gave the Molisch reaction, and reduced ammoniacal silver nitrate, but it did not reduce Fehling's solution even on boiling. In alcoholic solution, it was feebly laevorotatory; for  $c = 5.002$ , and  $l = 1$ ,  $\alpha_D^{20} = -0.7^{\circ}$ , hence  $[\alpha]_D^{20} = -13.99^{\circ}$ .

The neutral oil, which yielded the crystals of pentamethylated glucose, was recovered from the porous tile by extraction with ether. It was indifferent to Fehling's solution, but the product of its hydrolysis, a viscid liquid which was isolated by the process used in previous cases, reduced this reagent on warming. A ligroin extract of the syrup, when evaporated, deposited crystals which, from their appearance and solubility in this solvent, were taken to be tetramethyl glucose. Their low melting point,  $55-57^{\circ}$ , much higher, however, than that of the above-mentioned pentamethylated derivative, may very well have been due to adhering oil from which it was impossible to free them on account of the minute quantity of the material. An explanation of the probable production of this substance is given in the introduction.



*Alkylation of Cane Sugar.*

The materials used in a preliminary experiment were: three grams of cane sugar (1 mol.), 20 grams of methyl iodide (20 mols.), and 16 grams of silver oxide (10 mols.). The sugar, previously dissolved in 3 c.c. of warm water, was mixed with 20 c.c. of pure methyl alcohol, and in order to avoid the precipitation of the sugar by the iodide and, as far as possible the oxidising effect of the oxide, the same precautions were taken in mixing the materials as in the methylation of methyl glucoside. A brisk reaction was set up on slightly warming. After all the iodide and oxide had been added, the mixture was heated for 4 hours on a water-bath under a reflux condenser, and then extracted with methyl alcohol. The residue left on evaporating the alcohol was a viscid, neutral oil, partially soluble in methyl iodide and dissolving readily in methyl alcohol. After being dried at 100° in a vacuum, this was dissolved in 10 c.c. of the latter liquid and the process of alkylation and extraction was repeated. The solubility of the substance in methyl iodide had now so far increased that only 2 c.c. of methyl alcohol were required to keep it in solution, and after a third alkylation with the same quantity of materials as before, ether could be used for the extraction of the product. On a fourth alkylation, it was found possible to dispense entirely with alcohol, and the reaction produced on adding the oxide was very feeble. The product, obtained as in previous alkylations, weighed 2 grams; it had a neutral reaction, was not very soluble in water, and did not reduce Fehling's solution. The decreasing weights of the silver residues from the successive alkylations, 32, 30, 28, and 22 grams respectively from 16 grams of oxide, showed that the conversion into iodide became less complete as the alkylation proceeded.

As the oil thus procured failed to crystallise, it was hydrolysed by boiling for half an hour with 50 c.c. of about 1·5 per cent. aqueous hydrochloric acid. The product of hydrolysis, obtained as in previous cases, was a yellow oil which, on being nucleated with tetramethyl glucose, deposited the long, crystalline needles characteristic of this substance. The crystals, after being dried on porous tile, recrystallised from ligroin, and left in a vacuum over paraffin wax, melted at 83—84°, the melting point previously found for tetramethyl glucose being 81—83°.

The tile used in absorbing the mother liquor of the crystals was extracted first with ligroin and then with ether. As neither extract crystallised on being nucleated, the material was again hydrolysed and treated as before, when an additional quantity of the crystalline needles was obtained. The total yield of crystals from the 2 grams of cane sugar ether was 0·32 gram.



The analysis of the crystals gave C = 50.72 ; H = 8.50 ; the required figures for tetramethyl glucose being C = 50.85 ; H = 8.47 per cent.

The uncrystallised part of the product of hydrolysis probably contains tetramethyl fructose, and the alkylation is being repeated on a larger scale with the view of isolating and identifying this substance.

We are applying our methods of alkylation to other members of the sugar group and to natural glucosides, and we purpose making a more complete study of the compounds already obtained, including their possible application to the synthesis of alkylated disaccharides.

In conclusion, we have to thank Mr. D. M. Paul and Mr. C. R. Young for zealous assistance given in the course of the research.

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### Cl.—Trimethyl $\alpha$ -Methylglucoside and Trimethyl Glucose.

By THOMAS PURDIE, F.R.S., and ROBERT C. BRIDGETT, M.A., B.Sc.,  
Berry Scholar in Science.

It is shown in the preceding paper that when  $\alpha$ -methylglucoside in methyl alcoholic solution is treated with silver oxide and methyl iodide, partial methylation of the compound occurs, the chief product of the reaction being a trimethylated  $\alpha$ -methylglucoside. The following experiments were undertaken with the view of supplementing and extending the observations on this compound which are therein recorded.

The method followed in preparing the substance was the same as that already described, but, with the idea of increasing the yield, a larger proportion of alkylating agent was employed. Using 35 grams of  $\alpha$ -methylglucoside (1 mol.), 252 grams of silver oxide (6 mols.), 309 grams of methyl iodide (12 mols.), and methyl alcohol in quantity just sufficient to dissolve the glucoside, the crude product obtained on distillation (b. p. 141—166° under 10—12 mm. pressure) weighed 27.4 grams, a quantity much in excess of the yield previously recorded. After several fractionations, however, only 9.7 grams of approximately pure trimethyl methylglucoside (b. p. 157° under 9 mm. pressure) were collected ; the yield was thus about 28 per cent. of the weight of glucoside taken. Analysis of the substance and an estimation of

methoxyl gave : C = 50.50, H = 8.33,  $\text{CH}_3\text{O}$  = 51.67 per cent., the calculated numbers being respectively 50.85, 8.47, and 52.54.

The most volatile fraction was collected at 138—140° and weighed 1.6 grams; it was much more mobile than the rest of the distillate, and evidently consisted chiefly of tetramethyl methylglucoside. When hydrolysed and treated in the manner previously described, it yielded, in fact, the well-defined tetramethyl glucose melting at 83°. The bulk of the distillate was in the less volatile fractions and consisted of ethers less highly methylated than the trimethyl glucoside. Despite the large quantity of alkylating material used, the methylation was therefore very incomplete. Analysis of the silver residues showed, nevertheless, that the silver oxide and methyl iodide had almost completely reacted. By extracting these successively with dilute sulphuric and nitric acids and by estimating the silver in each extract and weighing the residual iodide, it was found that of the oxide used only 1.9 per cent. was unaltered or converted into a compound soluble in sulphuric acid, 1.6 per cent. had become reduced to metallic silver, whilst 96.5 per cent. was converted into iodide. The loss of alkylating material was due to the production of dimethyl ether; a brisk evolution of the gas occurs in the course of the reaction, this ether being recognised by its inflammability and absorption by concentrated sulphuric acid, from which solvent it was evolved on dilution with water.

The production of dimethyl ether appears to be due not to the direct action of methyl iodide on silver oxide but to the methylation of the solvent methyl alcohol by these reagents. We find that when dry silver oxide is heated with an excess of methyl iodide there is no apparent change, but when anhydrous methyl alcohol is present the action starts immediately on warming and proceeds thereafter continuously without further heating. After 2 hours' heating on a water-bath under a reflux condenser, we found, by analysis of the silver residues, that in the former case only 35.5 per cent. of the oxide used was converted into iodide, whilst in the latter case 88 per cent. underwent this change. It appears probable that, if special precautions were taken to exclude moisture, methyl iodide and silver oxide in the absence of alcohol or substances of an alcoholic nature would not react, and that the well-known formation of ethers from the interaction of this oxide and alkyl iodides is due to the catalytic effect of traces of water, alcohols being thus first produced and afterwards alkylated. Erlenmeyer (*Annalen*, 1863, 126, 306) suggests this explanation of the formation of isopropyl ether from the interaction of moist silver oxide and isopropyl iodide.

The specific rotation of the trimethyl  $\alpha$ -methylglucoside in an approximately 5 per cent. solution in ethyl alcohol was  $[\alpha]_D^{20} +148.7^\circ$ , and after redistillation 150.2°, a number much in excess of the value



126.8°, found for the preparation described in the preceding paper. The  $\alpha$ -methylglucoside employed in the previous experiments was prepared by ourselves by Fischer's method; the material used in this research was supplied by Kahlbaum. This, however, could scarcely be the cause of this discrepancy, as the melting points of the two specimens, 165—167° and 164°, also the respective rotations in 5 per cent. aqueous solutions, namely,  $[\alpha]_D^{20} + 159.2^\circ$  and  $159.8^\circ$ , neither differed materially from each other nor from Fischer's data (*Ber.*, 1893, 26, 2406), these being 165—166° and  $[\alpha]_D^{20} + 157.5^\circ$  in a 10 per cent. solution for the melting point and specific rotation respectively.

In order to ascertain whether the tetramethyl  $\alpha$ -methylglucoside and the product of its hydrolysis, tetramethyl glucose, when prepared from Kahlbaum's material, would also show a higher optical activity than the specimens of these compounds previously obtained, their preparation from the  $\alpha$ -methylglucoside in question was carried out, the methods and the proportion of materials being the same as those given in the preceding paper. The specific rotation of the tetramethyl  $\alpha$ -methylglucoside was found to be  $+152.6^\circ$ , the highest rotation previously observed being  $140.5^\circ$ . The only explanation of the varying activity of the methylated  $\alpha$ -glucosides which we can offer at present is that already suggested, namely, that under the action of the methyl iodide, intramolecular rearrangement occurs, resulting in the production in varying amounts of the  $\beta$ -stereoisomerides. As  $\beta$ -methylglucoside is levorotatory, its methylated derivatives will be also levorotatory, or at all events much less dextrorotatory than the corresponding  $\alpha$ -derivatives, and the presence of the former, even in small quantity, would greatly lower the rotation.

The specific rotation of the tetramethyl glucose procured from the more active tetramethyl  $\alpha$ -methylglucoside gave, in an approximately 5 per cent. aqueous solution,  $[\alpha]_D^{20} + 87.7^\circ$ , the highest number previously found being  $83^\circ$ ; the difference in activity is less marked in this case. This was to be expected if the above explanation is correct, for supposing the methylated glucose to be capable of existing in the stereoisomeric  $\alpha$ - and  $\beta$ -forms, mixtures of these in any proportion would, when dissolved, probably soon attain the same condition of equilibrium and exhibit a constant rotation.

#### *Trimethyl Glucose.*

This compound was obtained by hydrolysing 7 grams of trimethyl  $\alpha$ -methylglucoside with dilute hydrochloric acid, the method followed being the same as in the preparation of tetramethyl glucose described in the preceding paper. On evaporating the dry ethereal solution, the



product (5 grams) had the appearance of a nearly colourless, viscid syrup which did not crystallise, even after a long time. It distilled, however, without apparent decomposition at about  $194^{\circ}$  under 9 mm. pressure, the following analytical results being obtained from the distillate:

0.2002 gave 0.3599  $\text{CO}_2$  and 0.1438  $\text{H}_2\text{O}$ .  $\text{C} = 49.03$ ;  $\text{H} = 7.98$ .

$\text{C}_9\text{H}_{18}\text{O}_6$  requires  $\text{C} = 48.65$ ;  $\text{H} = 8.11$  per cent.

A determination of methoxyl showed that the glucosidic alkyl group only had been removed by the hydrolysis:

0.1897 gave 0.614 AgI.  $\text{CH}_3\text{O} = 42.72$ .

$\text{C}_6\text{H}_9\text{O}_3(\text{OCH}_3)_3$  requires  $\text{CH}_3\text{O} = 41.89$  per cent.

To determine the specific rotation, 0.7574 gram of the distilled substance was dissolved in methyl alcohol and the solution made up to 20 c.c. at  $20^{\circ}$ . The observed rotation in a 2 dm. tube was  $+6.0^{\circ}$ , hence  $[\alpha]_D^{20} + 79.2^{\circ}$ . The substance is soluble in water and in the ordinary organic solvents, although not so soluble in ether as trimethyl methylglucoside. It reduces Fehling's solution in the cold and ammoniacal silver nitrate when slightly warmed; its aqueous solution becomes yellow and then brown on boiling with alkali, and with  $\alpha$ -naphthol and concentrated sulphuric acid (Molisch reagent) it gives the colorations characteristic of the reducing sugars. The behaviour of the substance with phenylhydrazine was not conclusive; an emulsion was produced when a solution of the acetate of the base was added to an aqueous solution of the sugar derivative, but the oily product could not be made to crystallise.

To obtain more decisive evidence of the aldehydic nature of the trimethyl glucose, it was oxidised with bromine water; 6.5 grams of bromine were added gradually to 3.25 grams of the methylated glucose dissolved in 16 grams of water, and after remaining overnight the solution was freed from bromine by boiling, and from hydrobromic acid by shaking with silver oxide, the dissolved silver being afterwards removed with sulphuretted hydrogen. The filtered liquid, on being evaporated to dryness, left a residue containing some barium salt produced from the barium carbonate present as an impurity in the silver oxide used. On evaporating an ethereal extract of this residue, 2.5 grams of a viscid oil were obtained which had only a slightly acid reaction. The acid resulting from the oxidation had apparently been transformed into lactone; this substance distilled without apparent decomposition at about  $160^{\circ}$  under 11 mm. pressure and was analysed, further purification being impossible. The results,  $\text{C} = 48.41$ ,  $\text{H} = 7.58$ , approximated to the numbers calculated for trimethylgluconolactone,  $\text{C} = 49.09$ ,  $\text{H} = 7.27$  per cent. An estima-

tion of methoxyl showed that these groups had not been removed by the treatment with bromine :

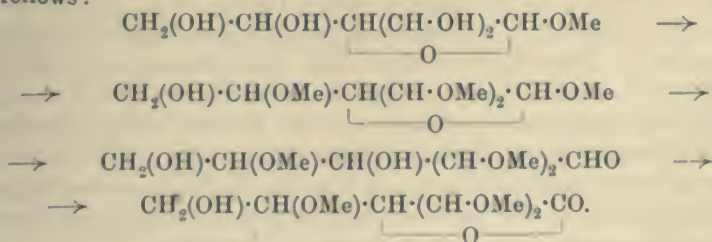
0.1500 gave 0.4909 AgI.  $\text{CH}_3\text{O} = 43.20$ .

$\text{C}_9\text{H}_{16}\text{O}_6(\text{OCH}_3)_3$  requires 42.27 per cent.

A barium salt was prepared from the substance, but it could not be obtained sufficiently pure for analysis. Evidence of the lactonic nature of the compound, however, was furnished by the gradual change of optical activity shown by its solution in aqueous alcohol, and by its behaviour on neutralisation with barium hydroxide. The specific rotation of a freshly prepared, approximately 4 per cent. aqueous alcoholic solution of the undistilled substance was found to be  $+76.5^\circ$ , and after 15 hours this diminished to  $+53.2^\circ$ .

An alcoholic solution containing 0.2251 gram of the substance, on being neutralised with aqueous barium hydroxide solution (1 c.c. = 0.01052 gram  $\text{Ba}(\text{OH})_2$ ), behaved precisely like the tetramethylgluconolactone described in the preceding paper. After each addition of the hydroxide, the pink colour of the phenolphthalein used as indicator disappeared slowly, and the solution again became distinctly acid. The colour of the indicator remained permanent after 8.15 c.c. of the barium hydroxide solution had been added;  $\text{C}_9\text{H}_{16}\text{O}_6$ , reckoned as lactone, requires 8.34 c.c. We conclude, therefore, that the substance was trimethylgluconolactone.

In the methylation of  $\alpha$ -methylglucoside, one of the carbinol groups is acted on more slowly than the others. Assuming this to be the terminal primary carbinol, the reactions described may be represented as follows :



If the unmethylated group of the trimethyl  $\alpha$ -methylglucoside is the terminal primary carbinol, as we suppose, the methylated glucose obtained from it should give trimethylsaccharic acid on oxidation with dilute nitric acid. We carried out the oxidation, but besides oxalic acid obtained only a syrupy acid from which we did not succeed in obtaining crystalline salts.

## CII.—*The Composition of so-called Elæomargaric Acid.*

By TOKUHEI KAMETAKA.

THE oil of *Elæococca vernicia*, or Japanese wood oil, was first investigated by S. Cloëz (*Compt. rend.*, 1875, 81, 469; 1876, 82, 501; 1876, 83, 943), who, on saponifying the oil with alcoholic potash, obtained two acids, one of which was solid and the other liquid at the ordinary temperature. At first, he gave the formula  $C_{17}H_{30}O_8$  to the solid acid, which he named *margarolic acid*, but in his third paper he changed the formula to  $C_{17}H_{30}O_2$ , having found that the earlier formula was incorrect owing to some absorption of oxygen by the acid having been overlooked. He also changed the name of the acid to *elæomargaric acid*. The liquid acid, which he at first named *elæolic acid*, was afterwards found to be ordinary oleic acid, the oil containing about 75 per cent. of the glyceride of elæomargaric acid and 25 per cent. of olein.

From the analysis and the determination of the neutralisation number, K. Ishikawa (*Dissertation*, 1885, unpublished) gave the formula  $C_{17}H_{28}O_2$  to the solid acid, whilst De Negri and Sburlati (*L'Orosi*, 1896, 19, 291) adopted Cloëz's formula,  $C_{17}H_{30}O_2$ .

In 1899, K. Higuchi (*Journ. Chem. Ind., Tokyo*, 2, 1), by oxidising the solid acid with potassium permanganate in an alkaline solution, obtained, besides dihydrostearic acid, a product which resembled sativic acid in many respects, but which he did not further examine. Quite recently, L. Maquenne (*Compt. rend.*, 1902, 135, 696) has published a paper "On the solid acid from the oil of *Elæococca vernicia*," in which he endeavoured to show that the composition of the acid is  $C_{18}H_{30}O_2$  rather than  $C_{17}H_{30}O_2$ , as given by Cloëz, and that the acid must therefore be stereoisomeric with linolenic acid. He arrived at this conclusion merely from the analysis of the acid, and stated that on account of the acid not forming any definite derivatives, its composition cannot be established by indirect means, his attempt to prepare the bromine additive product having failed.

The present communication is a preliminary report of an investigation, begun in 1901 and still in progress, which has for its object the determination of the composition of the acids of the oil by studying their oxidation and bromine additive products.

Although the work is still incomplete, it is desirable, in view of the appearance of Maquenne's paper, that the results should at once be published. A bromine additive product having the formula  $C_{14}H_{32}O_2Br_4$  was prepared without any difficulty from the mixture of acids produced by saponifying the oil, and from the recrystallised solid



acid were isolated oxidation products having the formulæ  $C_{18}H_{32}(OH)_4O_2$  and  $C_{18}H_{34}(OH)_3O_2$ , but no derivatives of either of the acids  $C_{17}H_{30}O_2$  or  $C_{18}H_{30}O_2$  could be obtained.\* If the acid  $C_{18}H_{30}O_2$  had been present in the mixture, as is asserted by Maquenne, the oxidation product,  $C_{18}H_{30}(OH)_4O_2$ , might have been expected, and should have been obtained in the course of a systematic separation of the products of oxidation (see experimental part). The principal acids of the oil appear, therefore, to be oleic acid and a solid acid having the formula  $C_{18}H_{32}O_2$ , stereoisomeric with linolic acid, whilst the presence in any considerable quantity of the acid  $C_{18}H_{30}O_2$  is excluded. The determination of the neutralisation number of the solid acid by means of carefully standardised alkali shows, moreover, that this corresponds with the formula  $C_{18}H_{32}O_2$  rather than with  $C_{17}H_{30}O_2$ .

No attempt was made to repeat the analyses of the solid acid, since no definite information was to be expected from the result on account of the small difference in the percentage amounts of carbon and hydrogen required by the formulæ  $C_{18}H_{32}O_2$ ,  $C_{18}H_{30}O_2$ , and  $C_{17}H_{30}O_2$ . The silver and lead salts of the solid acid were prepared, but they are both amorphous and very readily oxidisable in the air, even more so than the acid itself, so that, although silver estimations were made, no concordant results could be obtained. The reduction of the solid unsaturated acid by heating in a sealed tube with fuming hydriodic acid and red phosphorus has been tried, but the experiments in this direction have not yet been brought to a successful issue.

## EXPERIMENTAL.

### *Saponification of the Oil.*

To 30 grams of the cold-drawn oil contained in a flask were added 100 c.c. of alcohol and 15 grams of caustic potash, dissolved in 60 c.c. of water. The flask was connected with an inverted condenser and the contents gently boiled on the water-bath for about two hours. Hydrochloric acid was then added, in slight excess, to the clear alcoholic solution, when a brown oil separated, changing into a crystalline mass on cooling. By recrystallisation from alcohol, the solid acid was obtained in the form of white, lustrous laminae melting at  $43-44^\circ$  (Cloëz gives the melting point of the solid acid as  $48^\circ$ , whilst De Negri and Sburlati give it as  $43.8^\circ$ ).

*Bromine Additive Product.*—Fifty grams of the crude acid were, according to Hazura's method (*Monatsh.*, 1887, 8, 148), dissolved in 150 c.c. of glacial acetic acid, and to the solution, cooled by means of

\* In confirmation of the statement that no hexabromide can be obtained, see Walker and Warburton in the *Analyst*, 1902, 27, 238.

ice, 21 c.c. of bromine were gradually added with constant shaking; on thoroughly cooling the mixture, a crystalline precipitate separated out, together with some oily matter. After the precipitate had been repeatedly crystallised from glacial acetic acid and alcohol, its melting point was found to be  $114^{\circ}$ , which agrees with that of the bromine additive product of linolic acid,  $C_{18}H_{32}O_2$ . The bromine was estimated by Carius' method, with the following results:

I. 0.1830 gave 0.2279 AgBr. Br = 53.01.

II. 0.2702 „ 0.3381 AgBr. Br = 53.25.

$C_{18}H_{32}O_2Br_4$  requires 53.33; and  $C_{17}H_{30}O_2Br_4$ , 54.61 per cent.

On bromination, the pure recrystallised acid also gave a product melting at  $114^{\circ}$ , but its quantity was too small for a bromine estimation.

*Oxidation Products.*—From 75 grams of the crude acid, oxidised according to Hazura's method (*Monatsh.*, 1888, 9, 198), there were obtained two acids:

(1) A crude acid (4 grams), which, after purification by crystallisation, melted at  $171$ — $172^{\circ}$ ; determination of its neutralisation number led to the molecular weight 350.4 (sativic acid,  $C_{18}H_{32}(OH)_4O_2$ , = 348, melting point  $173^{\circ}$ ). The results of its combustion were as follows:

0.1329 gave 0.3015  $CO_2$  and 0.1214  $H_2O$ . C = 61.87; H = 10.16.

$C_{18}H_{32}(OH)_4O_2$  requires C = 62.07; H = 10.34 per cent.

(2) Another crude acid (1 gram) which, after recrystallisation from alcohol, melted at  $126^{\circ}$ , and had the molecular weight 317.3 (dihydroxystearic acid,  $C_{18}H_{34}(OH)_2O_2$ , = 316, melting point,  $136^{\circ}$ ). Probably, therefore, this substance is impure dihydroxystearic acid.

No characteristic crystals of either linusic or isolinusic acid,  $C_{18}H_{30}(OH)_6O_2$ , could be observed. The pure recrystallised solid acid (m. p.  $43$ — $44^{\circ}$ ) from the oil was dried over sulphuric acid in an atmosphere of carbon dioxide; a weighed quantity was dissolved in neutralised alcohol and titrated with 0.0568-normal sodium hydroxide solution, using phenolphthalein as indicator. The molecular weights found were 280.6, 277.1, and 280.9. Titrations with standard barium hydroxide solution gave the numbers 283.1 and 280.7, the mean of all the determinations being 280.5, whilst  $C_{18}H_{32}O_2$  = 280.

### *Summary of the Results.*

1. The principal organic acids of the oil of *Elæococca vernicia* are a solid acid, m. p.  $43$ — $44^{\circ}$ , and ordinary oleic acid, the former predominating.

2. The solid acid, which Cloëz named *elæomargaric acid*, and for which Maquenne recently proposed the name *α-elæostearic acid*, has the composition  $C_{18}H_{32}O_3$ , and not  $C_{17}H_{30}O_3$ , as calculated by Cloëz, or  $C_{18}H_{30}O_3$ , as given by Maquenne.

3. The solid acid is, undoubtedly, a stereoisomeride of linolic acid, the bromine additive product,  $C_{18}H_{32}O_2Br_4$ , as well as the oxidation product,  $C_{18}H_{32}(OH)_4O_2$ , obtained from the former, agreeing in every respect with those obtained from the latter.

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TOKYO.

### CHH.—Phosphoric Amidines.

By ROBERT MARTIN CAVEN.

IN the preparation of anilino-*p*-toluidinophosphoryl chloride (Trans., 1902, 81, 1369) by the interaction of anilinophosphoryl chloride and *p*-toluidine in benzene or ethereal solution, it was observed that the yield of the desired derivative was comparatively small and that a gummy mass separated from solution after crystallising the disubstituted compound. This mass was washed with alkali and then with dilute acid and subsequently crystallised from solution in dilute alcohol. The product thus obtained, after successive recrystallisations from alcohol containing a little water, yielded colourless needles which melted at  $188^\circ$ :

0.4156 gave 0.1871  $Mg_2P_2O_7$ .  $P = 12.55$ .

0.2800 „ 28.2 c.c. moist nitrogen at  $16^\circ$  and 759 mm.  $N = 11.74$ .

$C_{13}H_{13}ON_2P$  requires  $P = 12.70$ ;  $N = 11.48$  per cent.

This substance therefore appears to be phenyl-*p*-tolylphosphoric amidine,  $C_6H_5 \cdot NH \cdot PO \cdot N \cdot C_6H_4 \cdot CH_3$ .

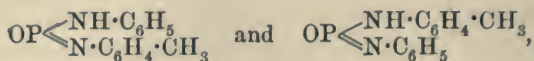
A similar compound to the above was obtained as a bye-product in the preparation of anilino-*p*-toluidinophosphoryl chloride from *p*-toluidinophosphoryl chloride and aniline, this substance being successively recrystallised until its melting point became constant at  $187$ — $188^\circ$ , and did not depress that of the preceding preparation:

0.2490 gave 23.5 c.c. moist nitrogen at  $11^\circ$  and 769 mm.  $N = 11.40$ .

$C_{13}H_{13}ON_2P$  requires  $N = 11.48$  per cent.

Thus, the two amidines, which, according to their mode of formation might be supposed to be

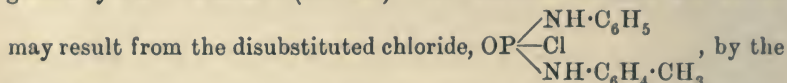




respectively, are indistinguishable.

This fact might be due to the lability of the aminic hydrogen atom, in which case it would constitute an example of "virtual tautomerism" (von Pechmann, *Ber.*, 1895, 28, 869, and 2362). Thus a condition of equilibrium might be attained in which the two isomerides would always be present in fixed proportion, whichever existed originally.

The identity may, however, be due to another cause, likewise suggested by von Pechmann (*loc. cit.*). An amidine such as the above



loss of hydrogen chloride, and since there is only one compound possessing this composition, the resulting product is likely to be the same whether it is a single substance or a mixture. In this case, since the two basic groups are very similar, it is probable that hydrogen would be removed with equal facility from either of them, and that a mixture of the two isomerides in more or less equal proportion would result.

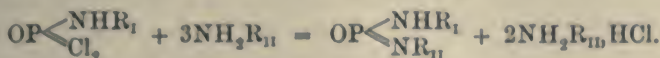
The problem presented by the above amidines is analogous to that studied by von Pechmann, except for the non-basic character of the phosphoric amidines.

Moreover, since a disubstituted chloride similar to that assumed to exist as an intermediate product by the theory of von Pechmann is known to be formed in the above reaction, this theory seems all the more probable in the present case. It becomes important, therefore, to ascertain, if possible, the conditions of formation of the amidine and more especially to determine whether the disubstituted chloride can pass into the amidine by removal of hydrogen chloride.

In order to discover whether the heat necessary to distil off the solvent was the cause of such transformation, anilino-*p*-toluidinophosphoryl chloride was dissolved in benzene and the solution heated for some time on the water-bath under an inverted condenser. The benzene was then distilled off and found to be quite free from hydrogen chloride, whilst the residue was completely soluble in dilute alkali. On the other hand, some amidine was formed when the disubstituted chloride was prepared, and the solvent removed in such a way that the temperature never rose above 45°. It appeared, therefore, that the amidine was not formed from the chloride by the operations involved in the removal of the solvent and subsequent treatment with alkali.

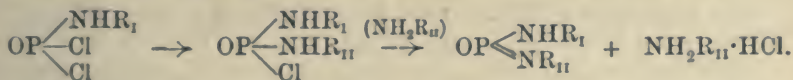
This conclusion would seem to warrant the suggestion that the

amidine is formed by the simultaneous replacement of the two chlorine atoms of the monosubstituted chloride according to the reaction



This condensation would be analogous with that obtaining in the case of thionyl chloride, which reacts with ethylamine to produce thionylethylamine,  $\text{SO}\cdot\text{N}\cdot\text{C}_2\text{H}_5$ , but it is doubtful whether either of these reactions is a simple one; it is still possible that the di-substituted phosphoryl chloride loses hydrogen chloride at the moment of its formation with the production of the amidine, although the reaction cannot be reproduced in the case of the crystallised compound.

In some of the later experiments, it was observed on adding the second amine to the benzene solution of the monosubstituted phosphoryl chloride that the separation of the hydrochloride formed as a bye-product was slow and partial, and at a certain point the solution became practically clear again. On allowing the liquid to remain for some hours, a sticky mass separated which contained most of the amidine, whilst the filtered benzene solution contained the di-substituted chloride. A consideration of these facts led to the hypothesis that the amidine is formed from the disubstituted chloride by the action of the added base, which first displaces a chlorine atom and then removes hydrogen chloride from the product, thus :



Michaelis and Silberstein (*Ber.*, 1896, 29, 716) have shown that disubstituted phosphoryl chlorides,  $(\text{RNH})_2\text{POCl}$ , when heated for some hours with boiling xylene, and then subsequently for an equal time at a somewhat higher temperature without a solvent, lose hydrogen chloride and yield products which are characterised by having high melting points and being insoluble in all solvents. These products are probably not simple amidines but polymeric substances containing a four- or six-membered ring of alternate phosphorus and nitrogen atoms.

In order to compare the properties of the simple amidines with the compounds obtained by Michaelis and Silberstein, the former were prepared in the same manner as the foregoing mixed amidine. Diphenyl- and di-*p*-tolyl-phosphoric amidines were obtained, but the yields were very poor, the products consisting almost entirely of the disubstituted derivatives.

The yield of amidine was, however, much increased by employing

metallic oxides in removing hydrogen chloride from the disubstituted chlorides. Four equivalents of aniline were added to one of phosphoryl chloride in benzene solution, and after removing the precipitated aniline hydrochloride the resulting solution of dianilino-phosphoryl chloride was heated on the water-bath for some time with rather more than an equivalent of dry silver oxide. A vigorous reaction took place and most of the chlorine was removed as silver chloride. Mercuric or magnesium oxide may be employed, but these reagents are less efficacious. This reaction, besides furnishing a convenient method of preparing phosphoric amidines, supports the foregoing theory that the removal of hydrogen chloride in the former experiments is due to the action of the substituting base itself.

Diphenylphosphoric amidine,  $C_6H_5 \cdot NH \cdot PO : N \cdot C_6H_5$ , crystallises from alcohol or glacial acetic acid in needles melting at  $225-226^\circ$ :

0.2532 gave 0.1198  $Mg_2P_2O_7$ .  $P = 13.19$ .

0.1158 „ 12.05 c.c. moist nitrogen at  $17^\circ$  and 759 mm.  $N = 12.08$ .

$C_{12}H_{11}ON_2P$  requires  $P = 13.48$ ;  $N = 12.17$  per cent.

The polymeride  $(C_6H_5 \cdot NH \cdot PO : NC_6H_5)_n$  of Michaelis and Silberstein melted at  $357^\circ$ .

Di-*p*-tolylphosphoric amidine,  $CH_3 \cdot C_6H_4 \cdot NH \cdot PO : N \cdot C_6H_4 \cdot CH_3$ , crystallises in needles melting at  $226-228^\circ$ :

0.2026 gave 17.7 c.c. moist nitrogen at  $10^\circ$  and 776 mm.  $N = 10.70$ .

$C_{14}H_{15}ON_2P$  requires  $N = 10.85$  per cent.

The polymeride  $(CH_3 \cdot C_6H_4 \cdot NH \cdot PO : N \cdot C_6H_4 \cdot CH_3)_n$  was found by Michaelis and Silberstein to melt at  $328^\circ$ .

Numerous attempts were made to determine the molecular weight of diphenylphosphoric amidine in solution, but without success. There can be little doubt, however, that these compounds are correctly represented by the simple molecular formula. They are thus related to the polymerides of Michaelis and Silberstein as ordinary metaphosphoric acid is related to di- or tri-metaphosphoric acid.

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#### CIV.—*Crystallised Ammonium Sulphate and the Position of Ammonium in the Alkali Series.*

By ALFRED EDWIN HOWARD TUTTON, D.Sc., F.R.S.

IN a previous communication (Trans., 1894, 65, 628), the author has described the morphological and physical properties of the crystallised normal sulphates of potassium, rubidium, and cesium; subsequently (*loc. cit.*, 1897, 71, 846), the results of a similar investigation of the corresponding selenates were described. A further memoir, presented to the Royal Society (*Phil. Trans.*, A, 1899, 192, 455), treated of the thermal deformation of the three sulphates. The general result of these investigations, as also of the study of a large number of double sulphates and selenates containing the same three alkali metals (Trans., 1893, 63, 337, and 1896, 69, 344; *Proc. Roy. Soc.*, 1900, 66, 248, and 1900, 67, 58; *Phil. Trans.*, A, 1901, 197, 255), has been to show that the entire morphological and physical properties of the crystals follow the order of progression of the atomic weights of the three alkali metals.

The present communication deals with the normal ammonium sulphate. The interest attaching to the determination of the effect of replacing an alkali metal by the radicle ammonium is obvious. It might have been thought that so common a substance as ammonium sulphate had long ago been exhaustively studied. This, however, is far from being the case, and the existing data are frequently contradictory and not infrequently quite inaccurate. Ammonium sulphate is not included among the large number of salts investigated by Topsøe and Christiansen.

#### *Deposition, Character, and Analysis of the Crystals.*

The crystals of ammonium sulphate employed in this work were obtained in cold, dry weather, under the ordinary atmospheric pressure, by very slow crystallisation of saturated, but not supersaturated, solutions; they were not prepared by forced evaporation *in vacuo*. Ammonium sulphate is distinctly hygroscopic in moist air, and on a damp day the faces of a crystal on the goniometer somewhat quickly show signs of being moist, the signal-images becoming rapidly blurred; in dry weather, however, the crystals used in this work have been found, on the conclusion of the measurements, which have usually occupied three or four days, to be almost unimpaired. The powdered salt, when exposed in thin films to the atmosphere in damp weather, soon becomes replaced by minute drops of saturated solution. It is, moreover, impossible to obtain crystals within a reasonable time from

a saturated solution by evaporation in moist air, but a change to dry weather, although unaccompanied by any appreciable lowering of the average temperature, induces a slow deposition of crystals, and those employed in the goniometry and the optical work were thus obtained.

Another curious property of the saturated solution of ammonium sulphate is that in small quantities it does not wet metallic or other hard surfaces, but rolls about over them in spherical drops resembling globules of mercury.

An estimation of the sulphuric anhydride present in a sample of the crystals was made as a guarantee of purity; 1.8295 grams of the crystals employed in the goniometrical and optical work yielded 3.2382 grams of barium sulphate, corresponding with 60.77 per cent. of sulphuric anhydride; the calculated percentage is 60.61.

The original stock, from which the solutions for crystallisation were prepared, had previously been purified by repeated recrystallisation from hot solution.

### *Solubility.*

The solubility of ammonium sulphate in water has been determined by Alluard (*Compt. rend.*, 1864, 59, 500), who found that the amount of salt dissolved by 100 grams of water at 0° is 71.0 grams; at 10°, 73.65; at 20°, 76.30; and so on, the solubility increasing regularly up to 100° by 2.65 grams for every 10°, the solubility at 100° being 97.50 grams. Alluard further noticed that a saturated solution boils at 107.5°.

In order that the author's work on this salt might be exactly comparable with that on the other salts of the series, a determination of solubility was made under precisely similar conditions. A saturated solution was employed which had remained in contact with deposited crystals for several days, in a crystallising dish placed under a bell-jar under the ordinary pressure, in order to minimise evaporation and to allow of the attainment of equilibrium between crystal and solution. The temperature being 8.2°, about 30 c.c. of this solution were decanted into a platinum basin and evaporated to dryness on a water-bath; the residual salt was further dried for six days in succession, on the first day at 80°, on the second at 100°, and the remainder of the time at 120° in an air oven, until it no longer lost weight. As ammonium sulphate melts at 140°, a higher temperature was not advisable. 55.8291 grams of this solution yielded 23.7068 grams of the anhydrous salt, hence 100 grams of water at 8.2° dissolve 73.8 grams of ammonium sulphate. This result corresponds fairly closely with that obtained by Alluard; his value for 8.2° would be 73.17.

*Specific Gravity of Aqueous Solutions of Ammonium Sulphate.*

The specific gravities of three solutions of accurately known strength were obtained in connection with the determinations to be subsequently described of the refraction constants of ammonium sulphate in the state of solution in water. They are appended below :

*Specific Gravities at 20° of Solutions of Ammonium Sulphate in Water compared with Water at 4°.*

| Percentage of salt present. | Sp. gr. |
|-----------------------------|---------|
| 40·64                       | 1·2339  |
| 40·35                       | 1·2334  |
| 35·00                       | 1·2030  |

Schiff (*Ann. Chem. Pharm.*, 1859, 110, 74) gives the value 1·2284 for a 40 per cent. solution, and 1·2004 for a 35 per cent. solution. These values are much lower than the author's as is also Schiff's value for the anhydrous salt.

*Goniometry.*

Fourteen excellent crystals were selected for the goniometrical measurements, from six different crops. Several of these crystals were of exceptional perfection, practically the whole of the very numerous faces affording perfect images of the signal-slit.

The accompanying table (p. 1052) exhibits the results of the measurements and calculations.

The *habit* of the salt is more or less tabular, parallel to the brachy-pinacoid  $b\{010\}$ .

The *ratio of the morphological axes* is

$$a : b : c = 0·5635 : 1 : 0·7319.$$

The *observed forms* were the following :

$$\begin{aligned} a &= \{100\} \infty \bar{P} \infty ; & b &= \{010\} \infty \bar{P}' \infty ; & c &= \{001\} oP ; & p &= \{110\} \infty P ; \\ p' &= \{130\} \infty \bar{P}3 ; & q &= \{011\} \bar{P} \infty ; & q' &= \{021\} 2\bar{P} \infty ; & q''' &= \{012\} \frac{1}{2} \bar{P} \infty ; \\ o &= \{111\} P ; & o' &= \{112\} \frac{1}{2} P. \end{aligned}$$

Mitscherlich (*Ann. Phys. Chem. Pogg.*, 1830, 18, 168) gives the measurements of two angles, namely,  $bq' = 34^{\circ}22'$  and  $ap = 29^{\circ}26'$ ; these are almost identical with the author's values,  $34^{\circ}20'$  and  $29^{\circ}24'$ . A table of the other angles of potassium sulphate is given, but only the two quoted angles for ammonium sulphate, with the statement that the rest are very similar to those of the potassium salt.



*Morphological Angles of Ammonium Sulphate.*

| Angle.  | Number<br>of measure-<br>ments.   | Limits.   | Mean<br>observed.   | Calculated.   | Differ-<br>ence.   |
|---|---|---|---|---|--|
| $\left\{ \begin{array}{l} ap = (100):(110) \\ pp' = (110):(130) \\ p'b = (130):(010) \\ pb = (110):(010) \\ pp = (110):(\bar{1}\bar{1}0) \end{array} \right.$   | $\left\{ \begin{array}{l} 4 \\ 35 \\ 37 \\ 36 \\ 22 \end{array} \right.$      | $\left\{ \begin{array}{l} 29^{\circ}20' - 29^{\circ}27' \\ 29\ 50 - 30\ 4 \\ 30\ 29 - 30\ 42 \\ 60\ 19 - 60\ 46 \\ 58\ 43 - 58\ 57 \end{array} \right.$     | $\left\{ \begin{array}{l} 29^{\circ}23' \\ 29\ 59 \\ 30\ 36 \\ 60\ 35 \\ 58\ 49 \end{array} \right.$  | $\left\{ \begin{array}{l} 29^{\circ}24' \\ 30\ 0 \\ 30\ 36 \\ 60\ 36 \\ 58\ 48 \end{array} \right.$   | $\left\{ \begin{array}{l} -1' \\ -1 \\ 0 \\ -1 \\ +1 \end{array} \right.$    |
| $\left\{ \begin{array}{l} cq''' = (001):(012) \\ q'''q = (012):(011) \\ cq = (001):(011) \\ qq' = (011):(021) \\ q'b = (021):(010) \\ qb = (011):(010) \end{array} \right.$   | $\left\{ \begin{array}{l} 4 \\ 3 \\ 37 \\ 30 \\ 34 \\ 41 \end{array} \right.$ | $\left\{ \begin{array}{l} 20\ 1 - 20\ 20 \\ 15\ 51 - 16\ 12 \\ 36\ 7 - 36\ 20 \\ 19\ 21 - 19\ 35 \\ 34\ 10 - 34\ 26 \\ 53\ 40 - 53\ 56 \end{array} \right.$ | $\left\{ \begin{array}{l} 20\ 9 \\ 16\ 3 \\ 36\ 12 \\ 19\ 27 \\ 34\ 20 \\ 53\ 48 \end{array} \right.$ | $\left\{ \begin{array}{l} 20\ 6 \\ 16\ 6 \\ 36\ 12 \\ 19\ 28 \\ 34\ 20 \\ 53\ 48 \end{array} \right.$ | $\left\{ \begin{array}{l} +3 \\ -3 \\ 0 \\ -1 \\ 0 \\ 0 \end{array} \right.$ |
| $\left\{ \begin{array}{l} ao = (100):(111) \\ oq = (111):(011) \\ oo = (111):(\bar{1}\bar{1}\bar{1}) \end{array} \right.$   | $\left\{ \begin{array}{l} 6 \\ 58 \\ 28 \end{array} \right.$                  | $\left\{ \begin{array}{l} 43\ 36 - 43\ 41 \\ 46\ 15 - 46\ 27 \\ 87\ 14 - 87\ 23 \end{array} \right.$  | $\left\{ \begin{array}{l} 43\ 39 \\ 46\ 21 \\ 87\ 18 \end{array} \right.$                             | $\left\{ \begin{array}{l} 43\ 39 \\ * \\ 87\ 18 \end{array} \right.$                                  | $\left\{ \begin{array}{l} 0 \\ - \\ 0 \end{array} \right.$                   |
| $ao' = (100):(112)$   | —   | —   | —   | 58 37   | —  |
| $\left\{ \begin{array}{l} bo = (010):(111) \\ oo = (111):(\bar{1}\bar{1}\bar{1}) \end{array} \right.$   | $\left\{ \begin{array}{l} 70 \\ 28 \end{array} \right.$                       | $\left\{ \begin{array}{l} 65\ 50 - 66\ 3 \\ 48\ 0 - 48\ 16 \end{array} \right.$   | $\left\{ \begin{array}{l} 65\ 56 \\ 48\ 7 \end{array} \right.$  | $\left\{ \begin{array}{l} 65\ 56 \\ 48\ 8 \end{array} \right.$  | $\left\{ \begin{array}{l} 0 \\ -1 \end{array} \right.$                       |
| $\left\{ \begin{array}{l} bo' = (010):(112) \\ o'o' = (112):(\bar{1}\bar{1}\bar{2}) \end{array} \right.$  | $\left\{ \begin{array}{l} - \\ - \end{array} \right.$                         | $\left\{ \begin{array}{l} - \\ - \end{array} \right.$   | $\left\{ \begin{array}{l} - \\ - \end{array} \right.$   | $\left\{ \begin{array}{l} 72\ 56 \\ 34\ 8 \end{array} \right.$  | $\left\{ \begin{array}{l} - \\ - \end{array} \right.$                        |
| $\left\{ \begin{array}{l} co' = (001):(112) \\ o'o = (112):(111) \\ co = (001):(111) \\ op = (111):(110) \\ o'p = (112):(110) \end{array} \right.$  | $\left\{ \begin{array}{l} 3 \\ 3 \\ 76 \\ 82 \\ 3 \end{array} \right.$        | $\left\{ \begin{array}{l} 36\ 35 - 36\ 42 \\ 19\ 21 - 19\ 35 \\ 56\ 3 - 56\ 14 \\ 33\ 42 - 33\ 59 \\ 53\ 16 - 53\ 25 \end{array} \right.$                   | $\left\{ \begin{array}{l} 36\ 39 \\ 19\ 28 \\ 56\ 9 \\ 33\ 51 \\ 53\ 22 \end{array} \right.$          | $\left\{ \begin{array}{l} 36\ 42 \\ 19\ 27 \\ 56\ 9 \\ * \\ 53\ 18 \end{array} \right.$               | $\left\{ \begin{array}{l} -3 \\ +1 \\ 0 \\ - \\ +4 \end{array} \right.$      |
| $\left\{ \begin{array}{l} po = (110):(\bar{1}\bar{1}\bar{1}) \\ oq' = (\bar{1}\bar{1}\bar{1}):(0\bar{2}\bar{1}) \\ qp = (0\bar{2}\bar{1}):(\bar{1}\bar{1}\bar{0}) \end{array} \right.$  | $\left\{ \begin{array}{l} 62 \\ 55 \\ 57 \end{array} \right.$                 | $\left\{ \begin{array}{l} 64\ 22 - 64\ 38 \\ 49\ 18 - 49\ 33 \\ 66\ 0 - 66\ 12 \end{array} \right.$   | $\left\{ \begin{array}{l} 64\ 30 \\ 49\ 24 \\ 66\ 6 \end{array} \right.$                              | $\left\{ \begin{array}{l} 64\ 31 \\ 49\ 24 \\ 66\ 5 \end{array} \right.$                              | $\left\{ \begin{array}{l} -1 \\ 0 \\ +1 \end{array} \right.$                 |
| $\left\{ \begin{array}{l} po' = (110):(\bar{1}\bar{1}\bar{2}) \\ o'q = (\bar{1}\bar{1}\bar{2}):(0\bar{1}\bar{1}) \\ pq = (110):(0\bar{1}\bar{1}) \\ qp = (0\bar{1}\bar{1}):(\bar{1}\bar{1}\bar{0}) \end{array} \right.$                         | $\left\{ \begin{array}{l} - \\ - \\ 65 \\ 68 \end{array} \right.$             | $\left\{ \begin{array}{l} - \\ - \\ 106\ 47 - 106\ 59 \\ 73\ 1 - 73\ 14 \end{array} \right.$  | $\left\{ \begin{array}{l} - \\ - \\ 106\ 52 \\ 73\ 8 \end{array} \right.$                             | $\left\{ \begin{array}{l} 71\ 58 \\ 34\ 13 \\ 106\ 51 \\ 73\ 9 \end{array} \right.$                   | $\left\{ \begin{array}{l} - \\ - \\ +1 \\ -1 \end{array} \right.$            |
| $\left\{ \begin{array}{l} p'o = (130):(111) \\ oo' = (111):(\bar{1}\bar{1}\bar{2}) \\ o'q' = (\bar{1}\bar{1}\bar{2}):(0\bar{2}\bar{1}) \\ oq' = (111):(0\bar{2}\bar{1}) \\ qp' = (0\bar{2}\bar{1}):(\bar{1}\bar{3}\bar{0}) \end{array} \right.$ | $\left\{ \begin{array}{l} 56 \\ - \\ - \\ 56 \\ 58 \end{array} \right.$       | $\left\{ \begin{array}{l} 43\ 53 - 44\ 7 \\ - \\ - \\ 91\ 4 - 91\ 28 \\ 44\ 32 - 44\ 52 \end{array} \right.$  | $\left\{ \begin{array}{l} 44\ 1 \\ - \\ - \\ 91\ 17 \\ 44\ 43 \end{array} \right.$                    | $\left\{ \begin{array}{l} 44\ 0 \\ 45\ 16 \\ 46\ 1 \\ 91\ 17 \\ 44\ 43 \end{array} \right.$           | $\left\{ \begin{array}{l} +1 \\ - \\ - \\ 0 \\ 0 \end{array} \right.$        |
| $\left\{ \begin{array}{l} p'o' = (130):(112) \\ o'q = (112):(0\bar{1}\bar{1}) \\ p'q = (130):(0\bar{1}\bar{1}) \\ qp' = (0\bar{1}\bar{1}):(\bar{1}\bar{3}\bar{0}) \end{array} \right.$  | $\left\{ \begin{array}{l} - \\ - \\ 52 \\ 53 \end{array} \right.$             | $\left\{ \begin{array}{l} - \\ - \\ 120\ 25 - 120\ 43 \\ 59\ 19 - 59\ 37 \end{array} \right.$   | $\left\{ \begin{array}{l} - \\ - \\ 120\ 33 \\ 59\ 27 \end{array} \right.$                            | $\left\{ \begin{array}{l} 58\ 50 \\ 61\ 43 \\ 120\ 33 \\ 59\ 27 \end{array} \right.$                  | $\left\{ \begin{array}{l} - \\ - \\ 0 \\ 0 \end{array} \right.$              |
| Total number of<br>measurements...  | 1222  |   |   |   |  |

Mitscherlich gives values for the ratio of the axes which, when recalculated according to the modern practice with  $b$  as unity, correspond with  $a:b:c=0.5643:1:0.7310$ .

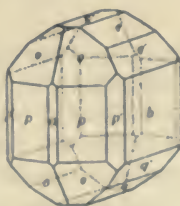
The spherical projection common to the whole series of sulphates and selenates of the alkali metals, and which is also applicable to ammonium sulphate, will be found on p. 852 of the selenate memoir (Trans., 1897, 71).

Crystals of ammonium sulphate which are grown rapidly in a single night by the cooling and slight evaporation of hot solutions, containing rather more than the amount of salt required for cold saturation, are usually of the form represented in Fig. 1.

FIG. 1.



FIG. 2.



This common type is not rich in faces, and is very markedly tabular parallel to the brachypinacoid  $b\{010\}$ .

Fig. 2 represents the more highly developed kind of crystal deposited slowly from cold saturated solutions under the conditions already specified.

The fourteen crystals measured were of this type. The brachypinacoid  $b\{010\}$  was invariably present and of some size, although not always large enough to give a tabular appearance to the crystal. Indeed, these more perfect, selected crystals were fairly equally developed as regards the  $b$  faces, those of the primary prism  $p\{110\}$  and of the two brachydomes  $q\{011\}$  and  $q'\{021\}$ . The faces of the second prism  $p'\{130\}$ , the primary pyramid  $o\{111\}$ , and the basal plane  $c\{001\}$  were usually smaller than those of the four forms just mentioned. The basal plane faces were not always both present, and one of the crystals measured showed only faint traces of either, but usually at least one  $c$  face was well developed and invariably yielded a perfect reflection. The orthopinacoid  $a\{100\}$  was the least developed of all the primary forms. On two of the crystals only were faces observed of sufficient size to afford good reflections. Generally mere linear traces were present. The faces of the pyramid  $o'\{112\}$  were only present on one of the selected crystals, and were exceedingly small, but afforded trustworthy reflections. Minute faces of the brachydome  $q''\{012\}$  also appeared on the same crystal.

Ammonium sulphate is, in general, less rich in faces than the sulphates and selenates of potassium, rubidium, and caesium. No trace was observed of the forms  $o\{332\}$ ,  $q\{031\}$ ,  $m\{102\}$ , or  $s\{132\}$ , which have been found on the crystals of those metallic salts.

In general habit, ammonium sulphate more closely resembles potassium sulphate than any other member of the series.

Triple twinning is frequent in the case of ammonium sulphate, as in the cases of the sulphate and selenate of potassium. Several such triplets were investigated, and found to be precisely similar in character to the well-known ones of potassium sulphate and those of potassium selenate (*loc. cit.*, p. 855).

### *Cleavage.*

There is one excellent cleavage developed in the crystals of ammonium sulphate, namely, parallel to the basal plane  $c\{001\}$ . This direction is also a plane of cleavage in the crystals of the sulphates and selenates of potassium, rubidium, and caesium. These metallic salts, however, exhibit a second cleavage direction, parallel to the brachypinacoid  $b\{010\}$ , and the cleavage along this plane is the more perfect one. No traces of such a cleavage could be discovered in the crystals of ammonium sulphate.

Groth (*Physikalische Krystallographie*, 3rd Ed., p. 396) gives the cleavage direction of ammonium sulphate as parallel to  $a\{100\}$ . As the order of the axes used by the author is the same as that employed by Groth, this is an error which has doubtless crept in owing to the confusion caused by the inversion of the order of Mitscherlich's axes (which is retained by Groth and the author) by Grailich and von Lang, who appear to have first observed the cleavage (*Sitzungsber. K. Akad. Wiss. Berlin*, 1858, 32, 53, and 33, 435 and 440).

Grailich and von Lang do not appear to have observed the other and more perfect cleavage exhibited by potassium sulphate parallel to the brachypinacoid  $b\{010\}$ . The fact that this latter cleavage is not developed in ammonium sulphate differentiates it from the sulphates and selenates of potassium, rubidium, and caesium, and is doubtless due to the very different atomic arrangement brought about by the replacement of a metal by the group  $\text{NH}_4$ .

### *Specific Gravity.*

Four determinations of the relative density were made by the method (pycnometer with cap) formerly employed for the sulphates and selenates of potassium, rubidium, and caesium. The crystals



chosen for the work were first powdered as finely as possible; the fineness was not very extreme, as the powder thus obtained was invariably slightly adhesive, partly owing to the small quantity of saturated solution which had previously been imprisoned in the usual minute cavities, and partly due to moisture attracted from the air. It was transferred to a platinum dish and heated for 2 days at  $80^{\circ}$ . The dry powder produced was then powdered much more finely, only such being accepted as passed through the meshes of a sieve of the finest platinum gauze. This powder of extreme tenuity was then further heated for a day at  $120^{\circ}$  in order to remove moisture either attracted from the air or released from cavities by the additional attrition; it was then sifted, the small quantity of coherent salt again powdered, and passed through the sieve, and finally the whole once more heated at  $120^{\circ}$  for 2 days.

The perfectly anhydrous powder thus obtained was transferred while hot to the pycnometers, which were then stoppered but not capped, allowed to cool in a desiccator, and capped when cold. Thus, the anhydrous salt, which was only momentarily in contact with the ordinary atmosphere, was then too hot to take up moisture. As crystallised ammonium sulphate melts at  $140^{\circ}$ , a higher temperature than  $120^{\circ}$  cannot with safety be employed in preparing the anhydrous salt without impairing the crystalline state.

Carbon tetrachloride was the liquid employed, as in the earlier investigations.

The following are the results of the observations :

*Specific Gravity of Ammonium Sulphate at  $20^{\circ}$ .*

| Weight of salt employed. | Sp. gr. at $20^{\circ}/4^{\circ}$ . |
|--------------------------|-------------------------------------|
| 5.1423 grams             | 1.7691                              |
| 5.5439 „                 | 1.7686                              |
| 5.6363 „                 | 1.7684                              |
| 4.8944 „                 | 1.7687                              |
|                          | <hr/>                               |
|                          | Mean 1.7687                         |

The earliest recorded determination of the specific gravity of ammonium sulphate, and one which is as remarkably near the truth as it is interesting, was carried out in Paris, in 1798, by "le citoyen" Hassenfratz, who at this time was associated with Berthollet. It is published in the *Annales de Chimie* (which preceded the *Ann. Chim. Phys.*), vol. 28, p. 3. The value obtained was 1.7676, and the method employed was similar in principle to the modern one of the pycnometer,

but the latter was of very large dimensions and weighed 262 grams. The liquid was mercury, the quantity required weighing 2018 grams; the air was eliminated under the receiver of a very large air pump.

Playfair and Joule determined the specific gravity of this salt twice. The first determination, made in the year 1845, gave the number 1.750 (*Memoirs Chem. Soc.*, 2, 423). The second and more elaborate determination, made in the year 1848, yielded the value 1.76147 at 4° (*Quart. Journ. Chem. Soc.*, 1, 138). It is interesting to note that the formula given in both these memoirs is  $\text{NH}_4\text{O}\cdot\text{SO}_3 + \text{HO}$ , which corresponds with the modern formula  $(\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}$ , the salt at that time being considered to contain a molecule of water of crystallisation. Schiff, in the year 1858 (*Ann. Chem. Pharm.*, 107, 64), obtained the number 1.628, a value which is unquestionably too low. Pettersson (*Nova Acta R. Soc. Scient. Upsaliensis*, 1874) found, as the mean of four experiments, the value 1.770, the limits being 1.7666 to 1.775 for 17.9° to 18.6°.

F. W. Clarke, in *Constants of Nature*, vol. 1, p. 79, quotes the value 1.765 for 20.5° as the result of a determination made by Wilson in his laboratory; Schröder (*Ber.*, 1878, 11, 2211) gives 1.773 as his latest determination.

Spring (*Ber.*, 1882, 15, 1940; and *Bull. Acad. roy. Belg.*, 1882, 4 197), using olive oil as the liquid, obtained the value 1.773 for 20°.

The mean of the results of the four most trustworthy previous determinations, namely, those of Playfair and Joule (1.761), Clarke (1.765), Schröder (1.773), and Pettersson (1.770) is 1.767, a value which is very close to that now obtained by the author (1.7687).

#### *Molecular Volume.*

The molecular volume, calculated from the author's value for the density, is:

$$V = M/d = \frac{132}{1.7687} = 74.63.$$

This is very close to the molecular volume, 74.56, given by Pettersson (*Ber.*, 1876, 9, 1559).

#### *Distance Ratios (Topic Axes).*

These ratios represent the relative distances apart,  $\chi$ ,  $\psi$ ,  $\omega$ , of the centres of the contiguous structural units of the crystals along the three rectangular directions of the crystallographic axes  $a$ ,  $b$ ,  $c$ . It was proved for the whole series of rhombic normal alkali sulphates and selenates in the memoir on "The nature of the structural unit"

(Traube, 1896, 69, 507), that the structural unit is a single chemical molecule. It should be mentioned that this conclusion, published by the author in 1896, agrees not only with the work of Fock, alluded to in the author's memoir, but also with the later research of Traube (*Ber.*, 1898, 31, 130), who, while criticising Fock's results concerning other series, himself shows that the structural unit of potassium sulphate and its analogues is indeed a single chemical molecule. The ratios, calculated from the formulæ

$$\chi = \sqrt{\frac{3}{a^2V}}, \quad \psi = \sqrt{\frac{3}{V}} \frac{1}{ac}, \quad \text{and} \quad \omega = \sqrt{\frac{3}{c^2V}} \frac{1}{a},$$

work out as follows :

$$\chi : \psi : \omega = 3.1873 : 5.6563 : 4.1398.$$

If the  $\psi$  value for potassium sulphate is taken as unity, as was done for the three metallic sulphates (Trans., 1894, 65, 659), the values for ammonium sulphate simplify to :

$$\chi : \psi : \omega = 0.5949 : 1.0558 : 0.7727.$$

### Optics.

The *plane of the optic axes* of ammonium sulphate is the brachypinacoid  $b\{010\}$ .

The *first median line* is the morphological axis  $a$

The *double refraction* is positive and small, requiring the preparation of thick section plates perpendicular to the first median line in order to obtain adequately small interference rings and sharp optic axial brushes for accurate measurement of the optic axial angle.

*Refractive Indices.*—The direction of the vertical morphological axis  $c$  is, in accordance with the above, the minimum axis  $a$  of the optical indicatrix and the maximum axis  $\pi$  of the optical velocity ellipsoid, whilst the forward morphological axis  $a$  is that of the maximum axis  $\gamma$  of the indicatrix and of the minimum axis  $\epsilon$  of the velocity ellipsoid, the morphological axis  $b$  being the intermediate axis  $\beta$  and  $b$  of both ellipsoids.

Six excellent prisms were ground, each in the direction required by theory to afford two indices directly, with the aid of the cutting and grinding goniometer. Two afforded the  $\alpha$ - and  $\beta$ -values, another pair gave  $\beta$  and  $\gamma$ , and the remaining two furnished  $a$  and  $\gamma$ . The results are set forth in the accompanying table :



*Refractive Indices of Ammonium Sulphate.*

| Index.                                       | Nature of light. | Prisms 1 and 2. | Prisms 3 and 4. | Prisms 5 and 6. | Mean index. |
|--|------------------|-----------------|-----------------|-----------------|-------------|
| $\alpha$ .<br>Vibrations parallel to axis c. | Li               | 1.5178—5        | —               | 1.5179—8        | 1.5177      |
|  | C                | 1.5181—0        | —               | 1.5183—2        | 1.5182      |
|  | Na               | 1.5210—04       | —               | 1.5213—08       | 1.5209      |
|  | Tl               | 1.5238—4        | —               | 1.5239—5        | 1.5237      |
|  | F                | 1.5270—67       | —               | 1.5272—69       | 1.5270      |
|  | G                | 1.5316—6        | —               | 1.5321—18       | 1.5318      |
| $\beta$ .<br>Vibrations parallel to axis b.  | Li               | 1.5200—198      | 1.5198—200      | —               | 1.5199      |
|  | C                | 1.5206—2        | 1.5202—4        | —               | 1.5204      |
|  | Na               | 1.5234—0        | 1.5227—30       | —               | 1.5230      |
|  | Tl               | 1.5260—57       | 1.5256—9        | —               | 1.5258      |
|  | F                | 1.5294—89       | 1.5289—90       | —               | 1.5291      |
|  | G                | 1.5341—37       | 1.5338—43       | —               | 1.5340      |
| $\gamma$ .<br>Vibrations parallel to axis a. | Li               | —               | 1.5295—8        | 1.5299—7        | 1.5297      |
|  | C                | —               | 1.5300—2        | 1.5302—2        | 1.5302      |
|  | Na               | —               | 1.5326—32       | 1.5332—29       | 1.5330      |
|  | Tl               | —               | 1.5355—61       | 1.5361—59       | 1.5359      |
|  | F                | —               | 1.5393—5        | 1.5394—2        | 1.5394      |
|  | G                | —               | 1.5443—6        | 1.5446—4        | 1.5445      |

19.

The mean refractive index (mean of all three indices) for sodium light is 1.5256.

The intermediate index  $\beta$ , corrected for a vacuum (the correction being +0.0004), is expressed for any wave-length  $\lambda$  by the formula :

$$\beta = 1.5094 + \frac{511\,719}{\lambda^2} - \frac{894\,520\,000\,000}{\lambda^4} + \dots$$

The  $\alpha$ -values are also very closely reproduced by the formula if the constant 1.5094 is diminished by 0.0022, and the  $\gamma$ -values, if the same constant is increased by 0.0100.

The refractive indices of ammonium sulphate for lithium and sodium flames were determined in the year 1867 by Erofejeff (*Sitzungsber. K. Akad. Wiss. Berlin*, 55, 543) by means of three prisms parallel to the three morphological axes. The values obtained were as follows :

|          | Dispersive power | $\alpha$ . | $\beta$ . | $\gamma$ . |
|----------|------------------|------------|-----------|------------|
| Li ..... | .....            | 1.5177     | 1.5200    | 1.5289     |
| Na ..... | .....            | 1.5208     | 1.5232    | 1.5332     |

Five of these values agree within 0.0002 of the author's numbers.

*Alteration of Refraction by Increase of Temperature.*—The indices of refraction were determined at the temperature of 80° with three of

the prisms, affording respectively  $\alpha$  and  $\beta$ ,  $\beta$  and  $\gamma$ , and  $\alpha$  and  $\gamma$ . The following table represents the results.

*Refractive Indices of Ammonium Sulphate at 80°.*

|        | $\alpha$ . | $\beta$ . | $\gamma$ . |        | $\alpha$ . | $\beta$ . | $\gamma$ . |
|--------|------------|-----------|------------|--------|------------|-----------|------------|
| Li ... | 1.5146     | 1.5174    | 1.5258     | Tl ... | 1.5206     | 1.5233    | 1.5320     |
| C ...  | 1.5151     | 1.5179    | 1.5263     | F ...  | 1.5239     | 1.5266    | 1.5355     |
| Na...  | 1.5178     | 1.5205    | 1.5291     | G ...  | 1.5287     | 1.5315    | 1.5406     |

On heating the crystals to 80°,  $\alpha$  diminishes by 0.0031,  $\beta$  by 0.0025, and  $\gamma$  by 0.0039. For Na-light the amount of double refraction at the ordinary temperature ( $\gamma - \alpha$ ) is 0.0121, but at 80° it becomes diminished to 0.0113. That is, the  $\alpha$  and  $\gamma$  values approach each other to the extent of 0.0008. The  $\beta$  and  $\gamma$  values, however, approach each other more than this, the difference between them for Na-light of 0.0100 at the ordinary temperature falling to 0.0086 at 80°, indicating an approach of 0.0014. On the other hand, the  $\alpha$  and  $\beta$  indices recede from each other, the difference for Na-light of 0.0021 at the ordinary temperature increasing to 0.0027 at 80°. There is thus a recession of 0.0006.

Hence, whilst all three refractive indices diminish with rise of temperature, they do not change equally. On the contrary, the amounts of change for the three indices are considerably different, and are such as result in the  $\beta$  index moving relatively nearer to the  $\gamma$  index, as well as in a diminution in the total amount of the double refraction  $\gamma - \alpha$ .

The relative movement of  $\beta$  nearer to  $\gamma$  ought to be accompanied by an increase of the optic axial angle. This will subsequently be shown to be the case.

*Axes of the Optical Indicatrix.*

|                             | $\gamma$ .                          | $\beta$ . | $\alpha$ . |
|-----------------------------|-------------------------------------|-----------|------------|
| At the ordinary temperature | $a : b : c = 1.0066 : 1 : 0.9986$ . |           |            |
| At 80° .....                | $a : b : c = 1.0057 : 1 : 0.9982$ . |           |            |

*Axes of the Optical Velocity Ellipsoid.*

|                             | $c$ .                               | $b$ . | $a$ . |
|-----------------------------|-------------------------------------|-------|-------|
| At the ordinary temperature | $a : b : c = 0.9935 : 1 : 1.0014$ . |       |       |
| At 80° .....                | $a : b : c = 0.9944 : 1 : 1.0018$ . |       |       |

The effect of rise of temperature in bringing the intermediate velocity of light transmission for the direction of the morphological

axis  $b$  nearer to the velocity along the axis  $a$  and relatively further from that along the vertical axis  $c$  is clearly shown by these ratios for the two temperatures.

*Molecular Optical Constants.*—The values of these constants are as follows:

| Morphological axis.   | $a.$  | $b.$  | $c.$  |
|---|---|---|---|
| Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n \dots$                 | $\left\{ \begin{array}{l} C \\ G \end{array} \right. \begin{array}{l} 0.1748 \\ 0.1787 \end{array}$ | $\begin{array}{l} 0.1721 \\ 0.1759 \end{array}$ | $\begin{array}{l} 0.1715 \\ 0.1753 \end{array}$ |
| Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m \dots$ | $\left\{ \begin{array}{l} C \\ G \end{array} \right. \begin{array}{l} 23.07 \\ 23.59 \end{array}$   | $\begin{array}{l} 22.72 \\ 23.21 \end{array}$   | $\begin{array}{l} 22.64 \\ 23.13 \end{array}$   |
| Specific dispersion, $n_a - n_c \dots \dots \dots$                      | 0.0039  | 0.0038  | 0.0038  |
| Molecular dispersion, $m_a - m_c \dots \dots \dots$                     | 0.52  | 0.49  | 0.49  |
| Molecular refraction, $\frac{n-1}{d} M \dots \dots \dots C$             | 39.60   | 38.87   | 38.70   |

The mean molecular refraction  $\frac{n-1}{d} M$  for ray  $C$  (mean of all three values for the three morphological axes of the crystals) is 39.06.

This latter value will presently be compared with the molecular refraction of ammonium sulphate in the state of solution in water.

*Optic Axial Angle.*—Three pairs of excellent section plates were prepared with the aid of the cutting and grinding goniometer, parallel to the first and second median lines. The accompanying tables show the results of the measurements obtained with them, of the angle in air 2E, and of the acute and obtuse angles 2Ha and 2Ho, as observed when the sections were immersed in  $\alpha$ -bromonaphthalene, together with the calculated values of the true optic axial angle 2Va derived from the two latter measurements.

*Apparent Optic Axial Angle in Air of Ammonium Sulphate.*

| Nature of light. | Section 1. | Section 2. | Section 3. | Mean 2E. |
|------------------|------------|------------|------------|----------|
| Li               | 84°44'     | 83°52'     | 83°27'     | 84° 1'   |
| C                | 84 44      | 83 53      | 83 28      | 84 2     |
| Na               | 84 46      | 83 56      | 83 35      | 84 6     |
| Tl               | 84 48      | 83 59      | 83 43      | 84 10    |
| F                | 84 50      | 84 4       | 83 52      | 84 15    |



*True Optic Axial Angle of Ammonium Sulphate.*

| Nature of light. | No. of section perpendicular. 1M.L.                        | Observed values of 2Ha.  | No. of section perpendicular. 2M.L.                           | Observed values of 2Ho.   | Calculated values of 2Va.   | Mean 2Va. |
|------------------|--|--|---|---|---|-----------|
| Li               | $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$ | $\left\{ \begin{array}{l} 48^{\circ}12' \\ 47\ 42 \\ 47\ 33 \end{array} \right.$ | $\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$ | $\left\{ \begin{array}{l} 111^{\circ}18' \\ 111\ 21 \\ 111\ 12 \end{array} \right.$ | $\left\{ \begin{array}{l} 52^{\circ}38' \\ 52\ 11 \\ 52\ 5 \end{array} \right.$ | 52°18'    |
| C                | $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$ | $\left\{ \begin{array}{l} 48\ 8 \\ 47\ 39 \\ 47\ 31 \end{array} \right.$         | $\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$ | $\left\{ \begin{array}{l} 111\ 11 \\ 111\ 14 \\ 111\ 7 \end{array} \right.$         | $\left\{ \begin{array}{l} 52\ 36 \\ 52\ 10 \\ 52\ 4 \end{array} \right.$        | 52 17     |
| Na               | $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$ | $\left\{ \begin{array}{l} 47\ 52 \\ 47\ 22 \\ 47\ 15 \end{array} \right.$        | $\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$ | $\left\{ \begin{array}{l} 110\ 35 \\ 110\ 37 \\ 110\ 36 \end{array} \right.$        | $\left\{ \begin{array}{l} 52\ 32 \\ 52\ 5 \\ 51\ 58 \end{array} \right.$        | 52 12     |
| Tl               | $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$ | $\left\{ \begin{array}{l} 47\ 35 \\ 47\ 5 \\ 46\ 56 \end{array} \right.$         | $\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$ | $\left\{ \begin{array}{l} 109\ 53 \\ 109\ 53 \\ 109\ 52 \end{array} \right.$        | $\left\{ \begin{array}{l} 52\ 28 \\ 52\ 1 \\ 51\ 53 \end{array} \right.$        | 52 7      |
| F                | $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$ | $\left\{ \begin{array}{l} 47\ 12 \\ 46\ 41 \\ 46\ 32 \end{array} \right.$        | $\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$ | $\left\{ \begin{array}{l} 109\ 7 \\ 109\ 6 \\ 108\ 59 \end{array} \right.$          | $\left\{ \begin{array}{l} 52\ 20 \\ 51\ 53 \\ 51\ 46 \end{array} \right.$       | 52 0      |

Des Cloiseaux (*Nouvelles Recherches sur les Propriétés Optiques des Cristaux*, p. 97) records for 2E the value  $87^{\circ}44'$  for red, and  $88^{\circ}47'$  for blue light, the specific wave-lengths not being given.

Erofejeff (*Sitzungsber. K. Akad. Wiss. Berlin*, 1867, 55, 543) gives for 2E through red glass  $86^{\circ}30'$ , and for sodium light  $85^{\circ}29'$ . This order of dispersion for 2E is contrary to that given by Des Cloiseaux, and is now shown by the author to be incorrect. For 2Va, calculated from observations in oil of 2Ha and 2Ho, Erofejeff obtained  $53^{\circ}32'$  for red glass (no specific wave-length) and  $52^{\circ}58'$  for sodium light.

The three sections perpendicular to the first median line employed by the author were at least two millimetres thick, this thickness being required in order to obtain very small rings and sharp brushes. Otherwise, the very slight amount of dispersion ( $13'$  being the mean value between C and F of the spectrum) in the case of 2E could not have been determined with certainty.

The calculated values of 2Va also indicate slight dispersion ( $17'$  between C and F) of the true angle. In order to confirm the order of this small dispersion, search was made for a liquid possessing the same refractive index as the crystals. Such a liquid was found in chlorobenzene, the refractive index of which for sodium light is 1.5248, almost identical with the mean index (1.5256) of the crystals.

A pure specimen of this liquid, boiling at  $131.9^{\circ}$  and having a sp. gr. 1.1235, was kindly placed at the author's disposal by Dr. V. H. Veley, to whom sincere thanks are due.

As observed in chlorobenzene, the brushes exhibited by the sections perpendicular to the first median line were markedly red inside and blue outside, indicating the fact that the true angle  $2Va$  is indeed greater for red than for blue. Measurements for C and F light afforded angles practically identical with the calculated values of  $2Va$  for these wave-lengths, and indicating that the calculated amount of dispersion is very near the truth.

*Effect of Rise of Temperature on the Optic Axial Angle.*—Section 3 was heated to  $80^{\circ}$  (corrected for conduction of crystal holder) in air, when  $2E$  was observed to increase somewhat rapidly, as stated by Des Cloizeaux (*loc. cit.*), who heated a plate to  $70^{\circ}$ , but who does not give any measurements for the higher temperature.

At  $80^{\circ}$ , the angle was found to be  $12^{\circ}53'$  larger than at the ordinary temperature. This is in accordance with the indications already shown to be afforded by the changes of refraction along the three axial directions of the optical indicatrix on heating to  $80^{\circ}$ . On cooling to the ordinary temperature again, the angle was found, some hours subsequently, to have been permanently increased by  $54'$  by the heating operation.

#### *Refraction in the State of Solution in Water.*

It was considered important, in view of the interesting results obtained in the cases of the sulphates and selenates of the alkali metals, to determine the refraction equivalent of dissolved ammonium sulphate. Three independent determinations were therefore made, two with solutions nearly saturated, and another with a somewhat more diluted solution. A fully saturated solution at  $8.2^{\circ}$  contains 42.5 per cent. of ammonium sulphate. The degree of saturation will be apparent from the numbers given in the third column of the following table:

*Molecular Refraction of Ammonium Sulphate Dissolved in Water.*

| Weight of salt.   | Weight of water. | Percentage of salt in solution. | Sp. gr. of solution at 20°/4°. | Refractive index of solution.  | Molecular refraction of salt in the state of solution. |
|---|------------------|---------------------------------|--------------------------------|--|--|
| 12.5675   | 18.3552          | 40.64                           | 1.2339                         | $\left. \begin{array}{l} \text{Li } 1.3939 \\ \text{C } 1.3943 \\ \text{Na } 1.3968 \\ \text{Ti } 1.3989 \\ \text{F } 1.4016 \\ \text{G } 1.4056 \end{array} \right\}$ | 39.76  |
| 15.2841   | 22.5919          | 40.35                           | 1.2334                         | $\left. \begin{array}{l} \text{Li } 1.3930 \\ \text{C } 1.3934 \\ \text{Na } 1.3959 \\ \text{Ti } 1.3979 \\ \text{F } 1.4007 \\ \text{G } 1.4042 \end{array} \right\}$ | 39.53  |
| 7.8421  | 14.5625          | 35.00                           | 1.2030                         | $\left. \begin{array}{l} \text{Li } 1.3860 \\ \text{C } 1.3864 \\ \text{Na } 1.3885 \\ \text{Ti } 1.3906 \\ \text{F } 1.3931 \\ \text{G } 1.3968 \end{array} \right\}$ | 39.71  |
| Mean refraction equivalent for the state of solution in water ... |                  |                                 |                                |  | 39.67  |
| " " of the crystals .....   |                  |                                 |                                |  | 39.06  |
| Difference... ..  |                  |                                 |                                |  | +0.61  |

The same care was taken to obtain the perfectly anhydrous salt as in the case of the determinations of the sp. gr. of the crystallised salt, and the water employed had, of course, been previously boiled and cooled out of contact with the atmosphere. The determinations were made with the same 10 c.c. pycnometers as were used in ascertaining the density of the crystals.

From the comparison instituted at the foot of the table between the mean of the three values for the different solutions and the mean refraction equivalent for the crystals, it will be observed that the value for solution is larger by 0.61 than the mean value for the crystals. The latter is derived either by taking the mean of the refraction equivalents for the three directions of the morphological axes, or by calculating the refraction equivalent from the mean of all three refractive indices of the crystals, for the wave-length of C-light.





Comparative Table of Morphological Angles.

| Angle.                               | Potassium<br>sulphate. | Rubidium<br>sulphate. | Cæsium<br>sulphate. | Ammonium<br>sulphate. |
|--------------------------------------|------------------------|-----------------------|---------------------|-----------------------|
| $\{ap = (100) : (110)$               | 29°48'                 | 29°47'                | 29°44'              | 29°24'                |
| $\{pp' = (110) : (130)$              | 30 0                   | 30 0                  | 30 0                | 30 0                  |
| $\{p'b = (130) : (010)$              | 30 12                  | 30 13                 | 30 16               | 30 36                 |
| $\{q'' = (001) : (012)$              | 20 21                  | 20 31                 | 20 33               | 20 6                  |
| $\{q''q = (012) : (011)$             | 16 13                  | 16 18                 | 16 21               | 16 6                  |
| $\{q'' = (001) : (011)$              | 36 34                  | 36 49                 | 36 59               | 36 12                 |
| $\{qq' = (011) : (021)$              | 19 27                  | 19 26                 | 19 26               | 19 28                 |
| $\{q'b = (021) : (010)$              | 33 59                  | 33 45                 | 33 35               | 34 20                 |
| $ao = (100) : (111)$                 | 43 52                  | 43 41                 | 43 31               | 43 39                 |
| $ao' = (100) : (112)$                | 58 44                  | 58 31                 | 58 19               | 58 37                 |
| $bo = (010) : (111)$                 | 65 37                  | 65 33                 | 65 32               | 65 56                 |
| $bo' = (010) : (112)$                | 72 42                  | 72 37                 | 72 33               | 72 56                 |
| $\{co' = (001) : (112)$              | 36 44                  | 37 0                  | 37 13               | 36 42                 |
| $\{o'o = (112) : (111)$              | 19 27                  | 19 26                 | 19 25               | 19 27                 |
| $\{co = (001) : (111)$               | 56 11                  | 56 26                 | 56 33               | 56 9                  |
| $\{op = (111) : (110)$               | 33 49                  | 33 34                 | 33 22               | 33 51                 |
| $\{po = (110) : (1\bar{1}1)$         | 65 8                   | 65 2                  | 64 54               | 64 31                 |
| $\{oq' = (1\bar{1}1) : (0\bar{2}1)$  | 49 12                  | 49 22                 | 49 30               | 49 24                 |
| $\{q'p = (0\bar{2}1) : (1\bar{1}0)$  | 65 40                  | 65 36                 | 65 35               | 66 5                  |
| $\{p'o = (110) : (1\bar{1}2)$        | 72 23                  | 72 15                 | 72 7                | 71 58                 |
| $\{o'q = (1\bar{1}2) : (0\bar{1}1)$  | 34 50                  | 35 4                  | 35 15               | 34 53                 |
| $\{qp = (0\bar{1}1) : (1\bar{1}0)$   | 72 47                  | 72 41                 | 72 38               | 73 9                  |
| $\{p'o = (130) : (111)$              | 43 59                  | 43 49                 | 43 40               | 44 0                  |
| $\{oo' = (111) : (1\bar{1}2)$        | 45 47                  | 45 55                 | 46 1                | 45 16                 |
| $\{o'q' = (1\bar{1}2) : (0\bar{2}1)$ | 46 1                   | 46 12                 | 46 20               | 46 1                  |
| $\{q'p' = (0\bar{2}1) : (1\bar{3}0)$ | 44 13                  | 44 4                  | 43 59               | 44 43                 |
| $\{p'o' = (130) : (112)$             | 58 48                  | 58 35                 | 58 25               | 58 50                 |
| $\{o'q' = (112) : (0\bar{1}1)$       | 62 12                  | 62 36                 | 62 53               | 61 43                 |
| $\{qp' = (0\bar{1}1) : (1\bar{3}0)$  | 59 0                   | 58 49                 | 58 42               | 59 27                 |

Comparison of Morphological Axial Ratios.

|                         |             |                         |
|-------------------------|-------------|-------------------------|
| For potassium sulphate, | $a : b : c$ | $= 0.5727 : 1 : 0.7418$ |
| „ rubidium „            | $a : b : c$ | $= 0.5723 : 1 : 0.7485$ |
| „ cæsium „              | $a : b : c$ | $= 0.5712 : 1 : 0.7531$ |
| „ ammonium „            | $a : b : c$ | $= 0.5635 : 1 : 0.7319$ |

From the comparison of the crystallographical axial ratios which has been instituted in the above table, it will be evident that the ratios for ammonium sulphate, whilst sufficiently close to those of the

other salts to indicate true isomorphism, are differently related to those of potassium sulphate than are those of rubidium and caesium sulphates. For, the replacement of potassium by the radicle ammonium causes a change in the ratio  $a:b$  in the same sense as, but greater in amount than, when rubidium or caesium is interchanged for potassium, but a change in the ratio  $c:b$  in the opposite sense and to an intermediate extent to that effected by introducing rubidium and caesium.

### *Density and Molecular Volume.*

From the accompanying table of specific gravities, it will be evident that ammonium sulphate is the lightest member of the series. Its molecular volume, however, as shown in the next table, is just slightly greater than that of rubidium sulphate. The substitution of ammonium for potassium is accompanied by an increase in volume of 9.3, while that of rubidium for potassium gives rise to an increase of 8.4. The replacement of potassium by caesium brings about an increase of 19.8 :

|                   | Comparison of<br>specific gravities.<br>For 20°/4°. |                    | Comparison<br>of molecular<br>volumes. |
|-------------------|---|--------------------|--|
| Ammonium sulphate | 1.7687  | Potassium sulphate | 65.33                                  |
| Potassium „       | 2.6633  | Rubidium „         | 73.77                                  |
| Rubidium „        | 3.6113  | Ammonium „         | 74.63                                  |
| Caesium „         | 4.2434  | Caesium „          | 85.17                                  |

The increase of volume due to the substitution of ammonium for potassium was given by Pettersson as 9.19, a result nearly identical with that now presented.

### *Separation of Centres of Structural Units.*

A comparison of the relative distances apart of the centres of the contiguous crystallographical structural units, which have been shown for this series of salts to be the chemical molecules, measured along the three rectangular directions of the morphological axes, will be seen from the next table to reveal the interesting fact that the replacement of potassium by ammonium is accompanied by approximately the same amount of extension of the crystal structure along those three axes as is the substitution of rubidium for potassium. Along the axis  $a$ , the extension is practically identical for the two substitutions, being only 0.0006 greater for the ammonium substitution; along the  $b$  axis, the introduction of ammonium causes a change greater by 0.0173, but not nearly so great as when



*Comparison of Distance Ratios (Topic Axes).*

|                        |                                    |         |
|------------------------|------------------------------------|---------|
| For potassium sulphate | $\chi:\psi:\omega = 0.5727:1$      | :0.7418 |
| „ rubidium „           | $\chi:\psi:\omega = 0.5943:1.0385$ | :0.7773 |
| „ ammonium „           | $\chi:\psi:\omega = 0.5949:1.0558$ | :0.7727 |
| „ caesium „            | $\chi:\psi:\omega = 0.6214:1.0879$ | :0.8193 |

caesium is introduced, and along the *c* axis the extension is less by 0.0046 for the ammonium substitution than for the rubidium one. The average difference of extension brought about by the rubidium and ammonium substitutions,  $1/3(0.0006 + 0.0173 - 0.0046)$ , is thus +0.0044. On the whole, therefore, the ammonium sulphate molecule occupies, as regards its dimensions in space, a position in the series very close to rubidium sulphate, and just slightly outside it. The fact that this is only true for the average extension, and not for all three individual axial extensions, is another indication of the peculiar nature of the ammonium member of the series. The last two conclusions, regarding the volume of the molecule and its dimensions in space, are particularly interesting as showing that the replacement of the two metallic atoms of potassium by the ten atoms included in two  $\text{NH}_4$  groups is accompanied by only a very slightly larger increase in volume, and consequent extension of the molecular dimensions along the three axial directions than when the two potassium atoms are replaced by two rubidium atoms. Moreover, the change is nothing like so large as that which occurs when two caesium atoms are substituted for the two atoms of potassium.

This surprising result opens up two very important questions, namely, the arrangement of the atoms in the molecule and the closeness of the packing of the molecular structural units in the crystal edifice. It would appear to suggest either that the atoms in the molecule have a large range of motion inside the molecular dimensions, adequate, in fact, to admit of the introduction of eight additional atoms within the molecular structure without altering those dimensions appreciably more than when a mere substitution of rubidium for potassium atoms is effected, or that the structural molecular units are so loosely packed, that is, the amount of free space is so large compared with the amount of matter in the whole space defined by the distance ratios, that there is sufficient room for the increase of the material part of the molecule by the introduction of eight additional atoms without extending the separation of the centres of contiguous molecules more than when a metallic interchange occurs. Possibly both these contingencies have their counterpart in actual facts.

*Comparison of the Optical Properties.  
Comparative Table of Refractive Indices.*

| Axial direction. | Nature of light. | $K_2SO_4$ . | $Rb_2SO_4$ . | $(NH_4)_2SO_4$ . | $Cs_2SO_4$ . |
|------------------|------------------|-------------|--------------|------------------|--------------|
| <i>a</i>         | { Li             | 1.4924      | 1.5120       | 1.5297           | 1.5633       |
|                  | { C              | 1.4928      | 1.5124       | 1.5302           | 1.5637       |
|                  | { Na             | 1.4947      | 1.5144       | 1.5330           | 1.5662       |
|                  | { Tl             | 1.4967      | 1.5166       | 1.5359           | 1.5690       |
|                  | { F              | 1.4995      | 1.5194       | 1.5394           | 1.5725       |
|                  | { G              | 1.5024      | 1.5235       | 1.5445           | 1.5775       |
| <i>b</i>         | { Li             | 1.4912      | 1.5108       | 1.5199           | 1.5615       |
|                  | { C              | 1.4916      | 1.5112       | 1.5204           | 1.5619       |
|                  | { Na             | 1.4935      | 1.5131       | 1.5230           | 1.5644       |
|                  | { Tl             | 1.4955      | 1.5153       | 1.5258           | 1.5672       |
|                  | { F              | 1.4982      | 1.5181       | 1.5291           | 1.5706       |
|                  | { G              | 1.5012      | 1.5222       | 1.5340           | 1.5756       |
| <i>c</i>         | { Li             | 1.4950      | 1.5109       | 1.5177           | 1.5569       |
|                  | { C              | 1.4954      | 1.5113       | 1.5182           | 1.5573       |
|                  | { Na             | 1.4973      | 1.5133       | 1.5209           | 1.5598       |
|                  | { Tl             | 1.4994      | 1.5155       | 1.5237           | 1.5624       |
|                  | { F              | 1.5023      | 1.5183       | 1.5270           | 1.5660       |
|                  | { G              | 1.5052      | 1.5224       | 1.5318           | 1.5705       |

From the comparison of the refractive indices which is instituted in the foregoing table, it will be clear that ammonium sulphate occupies a position, as regards refraction, near that of rubidium sulphate and between that salt and caesium sulphate. This will be rendered even clearer by the following comparison of the values of the mean refractive index (mean of all three indices for each salt) for sodium light:

*Mean Refractive Indices.*

|                            |        |                          |        |
|----------------------------|--------|--------------------------|--------|
| For potassium sulphate ... | 1.4952 | For ammonium sulphate .. | 1.5256 |
| „ rubidium „               | 1.5136 | „ caesium „              | 1.5635 |

The results of a similar comparison at  $80^\circ$  are entirely analogous, so that, within the range of existence of the crystals (ammonium sulphate melts at  $140^\circ$ ), the conclusion just arrived at is independent of temperature.

The axial ratios of the optical indicatrix or its polar reciprocal, the optical velocity ellipsoid, calculated with reference to the value for the *b* axis of potassium sulphate as unity, may be expected to show a similar relationship. The latter series are compared in the following table:

*Comparison of the Axial Ratios of the Optical Velocity Ellipsoid.*

|                        |                         |           |
|------------------------|-------------------------|-----------|
| For $K_2SO_4$ .....    | $a:b:c = 0.9992:1$      | $:0.9975$ |
| „ $Rb_2SO_4$ .....     | $a:b:c = 0.9862:0.9871$ | $:0.9869$ |
| „ $(NH_4)_2SO_4$ ..... | $a:b:c = 0.9742:0.9806$ | $:0.9820$ |
| „ $Ca_2SO_4$ .....     | $a:b:c = 0.9536:0.9547$ | $:0.9575$ |

The position of ammonium sulphate in the isomorphous series is here clearly shown to be between rubidium and caesium sulphates, and in close proximity to that of rubidium sulphate.

*Comparison of the Molecular Optical Constants.*

From the comparison made in the following table of the specific and molecular optical constants, it will be observed that the specific refraction and dispersion of ammonium sulphate are considerably different from the corresponding constants of the three metallic salts, and the change produced by the substitution of ammonium for potassium lies in the opposite direction to that which accompanies the substitution of rubidium or caesium :

*Comparative Table of Molecular Optical Constants.*

| Axis.  |       | a.                   | b.     | c.     |        |
|--|-------|----------------------|--------|--------|--------|
| Specific refraction,<br>$\frac{n^2-1}{(n^2+2)d} = n_s$               | Ray C | $(NH_4)_2SO_4$ ..... | 0.1748 | 0.1721 | 0.1715 |
|  |       | $K_2SO_4$ .....      | 0.1092 | 0.1089 | 0.1096 |
|  |       | $Rb_2SO_4$ .....     | 0.0832 | 0.0830 | 0.0831 |
|  |       | $Ca_2SO_4$ .....     | 0.0767 | 0.0765 | 0.0759 |
|  | Ray G | $(NH_4)_2SO_4$ ..... | 0.1787 | 0.1759 | 0.1753 |
|  |       | $K_2SO_4$ .....      | 0.1110 | 0.1107 | 0.1115 |
|  |       | $Rb_2SO_4$ .....     | 0.0847 | 0.0845 | 0.0846 |
|  |       | $Ca_2SO_4$ .....     | 0.0782 | 0.0780 | 0.0774 |
| Molecular refraction,<br>$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ | Ray C | $K_2SO_4$ .....      | 18.99  | 18.96  | 19.08  |
|  |       | $Rb_2SO_4$ .....     | 22.16  | 22.12  | 22.13  |
|  |       | $(NH_4)_2SO_4$ ..... | 23.07  | 22.72  | 22.64  |
|  |       | $Ca_2SO_4$ .....     | 27.71  | 27.63  | 27.45  |
|  | Ray G | $K_2SO_4$ .....      | 19.31  | 19.27  | 19.40  |
|  |       | $Rb_2SO_4$ .....     | 22.57  | 22.52  | 22.53  |
|  |       | $(NH_4)_2SO_4$ ..... | 23.59  | 23.21  | 23.13  |
|  |       | $Ca_2SO_4$ .....     | 28.26  | 28.18  | 27.98  |



| Axis.   | Specific dispersion,<br>$n_a - n_c$ . |           |           | Axis.   | Molecular dispersion,<br>$m_a - m_c$ . |           |           |
|---|---------------------------------------|-----------|-----------|---|--|-----------|-----------|
|   | <i>a.</i>                             | <i>b.</i> | <i>c.</i> |   | <i>a.</i>                              | <i>b.</i> | <i>c.</i> |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . | 0·0039                                | 0·0038    | 0·0038    | K <sub>2</sub> SO <sub>4</sub> .....            | 0·32                                   | 0·31      | 0·32      |
| K <sub>2</sub> SO <sub>4</sub> .....              | 0·0018                                | 0·0018    | 0·0019    | Rb <sub>2</sub> SO <sub>4</sub> ...             | 0·41                                   | 0·40      | 0·40      |
| Rb <sub>2</sub> SO <sub>4</sub> ...               | 0·0015                                | 0·0015    | 0·0015    | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | 0·52                                   | 0·49      | 0·49      |
| Cs <sub>2</sub> SO <sub>4</sub> .....             | 0·0015                                | 0·0015    | 0·0015    | Cs <sub>2</sub> SO <sub>4</sub> ...             | 0·55                                   | 0·55      | 0·53      |

| Axis.   | Molecular refraction, $\frac{n-1}{d}M$ . |           |           |
|---|--|-----------|-----------|
|   | <i>a.</i>                                | <i>b.</i> | <i>c.</i> |
| K <sub>2</sub> SO <sub>4</sub> .....                  | 32·22                                    | 32·14     | 32·39     |
| Rb <sub>2</sub> SO <sub>4</sub> .....                 | 37·83                                    | 37·74     | 37·75     |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ..... | 39·60                                    | 38·87     | 38·70     |
| Cs <sub>2</sub> SO <sub>4</sub> .....                 | 48·05                                    | 47·89     | 47·50     |

As regards molecular refraction, the whole of these constants for ammonium sulphate are very close to those for rubidium sulphate, and very slightly higher. Hence, ammonium sulphate occupies with respect to molecular refraction a similar position to that which it has been shown to take up as regards the volume and dimensions of the structural molecular unit, namely, between rubidium and caesium sulphates, and much nearer to the former than to the latter. This fact is most clearly exhibited by a comparison of the mean values of the molecular refraction  $\frac{n-1}{d}M$  for the ray *C*, that is, the mean of all three values for the three morphological axial directions of each salt.

#### *Mean Molecular Refractions.*

|                            |       |  |                           |       |
|----------------------------|-------|--|---------------------------|-------|
| For potassium sulphate ... | 32·25 |  | For ammonium sulphate ... | 39·06 |
| „ rubidium „ ...           | 37·77 |  | „ caesium „ ...           | 47·81 |

A similar result is found in the case of the molecular dispersion, only the intermediate position is nearer to that of caesium sulphate.

Coming next to the refraction equivalent for dissolved ammonium sulphate, it has been shown that the value, 39·67, is slightly higher

than the mean refraction equivalent for the crystals given in the preceding table, the difference between the two being +0.61. It has been previously shown by the author (Trans., 1897, 71, 914) that the three metallic sulphates, as also the selenates, likewise exhibit slight differences between their refraction equivalents for the state of solution and the crystallised condition, and that these differences exhibit an interesting progression, from a positive difference exceeding a unit in the case of the potassium salt to a small negative difference in the case of the caesium salt, the rubidium salt showing an intermediate small positive difference. Now, in the case of rubidium sulphate, this difference is +0.62, almost identical with that now found for ammonium sulphate, the minute difference of +0.01 being, as has so often been shown to be the case, on the side nearer to the value for the caesium salt. This fact will be more clearly apparent from the following table:

*Refraction Equivalents for Crystals and Solution.*

|                          | Mean mol. re-<br>fraction of<br>crystals. | Mol. refraction<br>of the<br>solution. | Diff. |
|--------------------------|---|--|-------|
| Potassium sulphate ..... | 32.25                                     | 33.39                                  | +1.14 |
| Rubidium „ .....         | 37.77                                     | 38.39                                  | +0.62 |
| Ammonium „ .....         | 39.06                                     | 39.67                                  | +0.61 |
| Caesium „ .....          | 47.81                                     | 47.57                                  | -0.24 |

The final conclusion as regards the specific and molecular refraction constants is, therefore, that whilst the more complex nature of the group  $\text{NH}_4$ , as compared with the simpler nature of the metallic atom which it is capable of replacing in this series of salts, is indicated and emphasised by the very different specific refraction and dispersion constants, yet, as regards the molecular constants, the ammonium radicle plays a part very similar to that of the rubidium atom.

It now remains to compare the orientation and angles of separation of the optic axes (bi-normals) of the four sulphates, which involves the consideration of the general optical scheme for the crystals of each salt.

In this series, the problem is an especially complex one, for the scheme is a different one for each salt. The author has shown, however, that, as in the case of the analogous selenates, it becomes perfectly simple when considered in connection with the axial ratios of the optical ellipsoids, in which the value along the  $b$  axis of each salt is taken as unity. These ratios naturally determine the loci of the circular sections of the optical ellipsoid, to which the optic axes (bi-normals) are perpendicular.

These ratios for the sulphates are as follows:

|                        |                           |
|------------------------|---------------------------|
| For $K_2SO_4$ .....    | $a:b:c = 0.9992:1:0.9975$ |
| „ $Rb_2SO_4$ .....     | $a:b:c = 0.9991:1:0.9999$ |
| „ $Cs_2SO_4$ .....     | $a:b:c = 0.9989:1:1.0029$ |
| „ $(NH_4)_2SO_4$ ..... | $a:b:c = 0.9935:1:1.0014$ |

It was shown in the memoir on the alkali sulphates that the different orientation of the optic axes in the three metallic salts was the direct outcome of the regular progression exhibited by these ratios. Owing to the initial smallness of the double refraction and to the much more rapid change of the ratio  $c:b$  on replacing one metal by another of higher atomic weight, and to the direction of this change being that which still further reduces the double refraction, it is found that the substitution of rubidium for potassium gives rise to just that amount of reduction required to bring the ratio  $c:b$  practically to unity, and that the continuation of the operation when caesium is substituted renders the value of the ratio greater than unity, and so entirely reverses the optical scheme. Incidental phenomena concomitant with this reversal are the change in the character of the double refraction from positive, in potassium sulphate, to negative, in caesium sulphate, and the extraordinary optical character of rubidium sulphate, which exhibits crossed-axial-plane dispersion as the temperature is raised and simulates uniaxial optical symmetry about the temperature of  $50^\circ$  ( $39^\circ$  for Li-,  $63^\circ$  for G-light).

The very different character of the ammonium substitution is evident from the considerable change produced on the ratio  $a:b$ , which remained almost unaffected by the metallic substitutions, but some interesting facts will be apparent from a consideration of the general optical characters of the four salts, which are determined by these ratios.

#### *Comparison of General Optical Characters.*

| Salt.          | Range of temperature.              | Plane of optic axes. | Direction of first med. line. | Sign of double refraction. | Optical scheme. |
|----------------|------------------------------------|----------------------|-------------------------------|----------------------------|-----------------|
| $K_2SO_4$      | Throughout                         | $a(100)$             | axis $c$                      | +                          | $bac$<br>+      |
| $Rb_2SO_4$     | Ordinary temp. to $50^\circ$       | $c(001)$             | „ $a$                         | +                          | $cab$<br>+      |
|                | Between $50^\circ$ and $180^\circ$ | $b(010)$             | „ $a$                         | +                          | $cba$<br>+      |
|                | Above $180^\circ$                  | $b(010)$             | „ $c$                         | -                          | $cba$<br>-      |
| $(NH_4)_2SO_4$ | Throughout                         | $b(010)$             | „ $a$                         | +                          | $cba$<br>+      |
| $Cs_2SO_4$     | „                                  | $b(010)$             | „ $c$                         | -                          | $cba$<br>-      |

The intermediate character of rubidium sulphate, between the widely different potassium and caesium salts, which is so clearly



exhibited by the optical axial ratios, is also shown by this table, and on heating the crystals of rubidium sulphate above  $180^{\circ}$  this salt actually becomes optically similar to caesium sulphate. But if the crystals of rubidium sulphate are less intensely heated, namely, to a temperature only slightly exceeding  $50^{\circ}$ , they become precisely similar, optically, to those of ammonium sulphate. Moreover, this orientation of the optical ellipsoid is then retained over the relatively large range of temperature from  $50^{\circ}$  to  $180^{\circ}$ , above which higher limit the same orientation as that shown by the caesium salt is attained. Clearly, then, in this respect, ammonium sulphate stands between rubidium and caesium sulphates and much nearer to the former.

### *Summary of Conclusions.*

It has now been shown that, in the cases of nine out of the twelve properties which have been investigated, ammonium sulphate stands in the series of normal alkali sulphates between rubidium and caesium sulphates and very close to the rubidium salt. The nine properties for which this is true are: solubility in water, molecular volume, the average distances apart of contiguous molecules along the three axial directions, the refractive indices, the axial ratios of the optical ellipsoid, the directional molecular refraction, the mean refraction equivalent for the crystals, the refraction equivalent for the state of solution in water, and the general optical scheme which governs the optic axial angle phenomena. Thus, with regard to all these properties, the replacement of the two atoms of potassium by the ten atoms of the ammonium groups is accompanied by an effect but slightly greater than that produced when two atoms of rubidium are substituted for those of potassium.

In regard to the three remaining properties, the morphological angles, the morphological axial ratios, and the specific refraction, as well as certain details of the distance ratios and of the optic axial angle phenomena, and the development of cleavage along only one, instead of two, directions, the specifically different character of the ammonium radicle, as compared with the simple atoms of the alkali metals, asserts itself. Yet, even in the case of the crystallographical angles, this specific difference is only manifested as to the direction of the change of angle brought about by replacing potassium by ammonium, as compared with that due to the substitution of one alkali metal for another, and as regards the amount of the change the ammonium salt stands between the rubidium and caesium salts, and somewhat nearer to the latter. It is, indeed, surprising that the introduction of eight additional atoms should be accompanied by less change in the exterior angles of the crystals than when a mere substitution of caesium

atoms for potassium atoms occurs. The changes in the axial ratios are simply the natural consequence of those in the morphological angles. Indeed, the axial ratios may be considered as the specific, and the distance ratios, obtained by combining them with the molecular volume, as the molecular morphological constants. In regard to both morphology and optics, the specific constants indicate the peculiar nature of the  $\text{NH}_4$  radicle, whilst the molecular constants exhibit ammonium in its proper place in the alkali series, namely, immediately after rubidium.

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### CV.—*The slow Oxidation of Methane at low Temperatures. Part II.*

By WILLIAM A. BONE and RICHARD V. WHEELER.

IN an earlier paper (Trans., 1902, 81, 535), we described a series of experiments on the interaction of methane (2 volumes) and oxygen (1 volume) in borosilicate glass bulbs at temperatures between  $300^\circ$  and  $400^\circ$ , which showed that part of the methane was oxidised to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or deposition of carbon. Moreover, the process was always marked by a diminution in the pressure of the cold gaseous products corresponding approximately with the oxygen which had disappeared, and at the end of the reaction a considerable proportion of the original methane always remained intact.

Since, under the experimental conditions, the rate at which hydrogen and oxygen combine was shown to be inappreciable, and as we were unable to detect the formation of any product intermediate between the original gases and the carbon monoxide, carbon dioxide, and steam finally obtained, we concluded provisionally that the first distinguishable stage in the combustion of methane at low temperatures involves the simultaneous oxidation of the carbon and hydrogen to carbon monoxide and steam respectively, thus,  $2\text{CH}_4 + 3\text{O}_2 = 2\text{CO} + 4\text{H}_2\text{O}$ . But, as was then pointed out, this explanation did not account for the whole of the observed facts, and it could therefore only be regarded as a first approximation to the truth. In the first place, on *a priori* grounds, it was difficult to believe that the primary reaction between methane and oxygen could possibly be pentamolecular. A second, and more serious, difficulty was the fact that a not inconsiderable proportion of the carbon of the methane burnt always appeared as carbon dioxide in the final products (in several cases, the ratio  $\text{CO}_2 : \text{CO}$  exceeded 1 : 2, and occasionally it approximated to 1 : 1). Now, since the rate at which



carbon monoxide reacts with moist oxygen or with steam under the experimental conditions was shown to be negligible (*loc. cit.*, p. 538), this formation of carbon dioxide could not be explained by supposing that the carbon monoxide actually liberated during the primary reaction was subsequently oxidised through the agency of steam and oxygen or steam alone (p. 540).

Such considerations as these indicated the necessity of a closer study of the phenomena involved if we were ever to gain a clear insight into the mechanism of the oxidation of hydrocarbons; the present paper on methane, and another which we hope to publish shortly on ethane, will show how far we have succeeded in this direction.

Our earlier experimental method involved the use of borosilicate glass bulbs of somewhat limited capacity (70 c.c.); but whilst this method afforded us the indispensable conditions for proving certain points of fundamental importance (for example, that no free hydrogen is liberated during the whole course of the oxidation), it was not so well adapted for the detection and isolation of transient intermediate products, and indeed, as we have already stated, the method failed to reveal the formation of any such substances. For the second stage of the inquiry, we devised an apparatus which has enabled us to experiment with much larger volumes (about 1200 c.c.) of the mixture of methane and oxygen, to follow from day to day the pressure changes in the reacting gases, and to remove from the sphere of action small quantities of intermediate products before they underwent further oxidation.

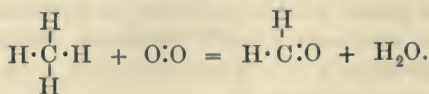
The results of these additional experiments, whilst they entirely confirm our previous conclusion that neither free hydrogen nor free carbon is produced at any stage of the oxidation, and that the final products consist simply of carbon monoxide, carbon dioxide, and steam, prove the transient formation of formaldehyde as an intermediate product. In one experiment, for instance, 13 per cent., and in another as much as 22 per cent., of the methane burnt was accounted for as formaldehyde removed from the sphere of action before it had been further oxidised.

This new observation not only affords a simple explanation of the production of so much carbon dioxide in our earlier experiments, but it also throws a new light on the whole question under discussion, and enables us to arrive at a clearer understanding of the mode in which the methane molecule is attacked by the oxygen.

Reviewing now the whole of the evidence obtained during the course of our investigation, we are justified in concluding that the oxidation of methane involves at least two distinct and successive changes, each of a simple character, namely :

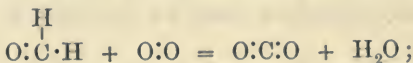


(1) The simultaneous production of formaldehyde and steam as the result of the bimolecular reaction :

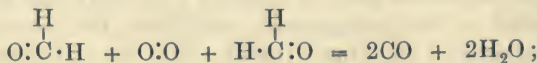


(2) The subsequent very rapid oxidation of the formaldehyde to carbon monoxide, carbon dioxide, and steam. This may be best considered as the result of two simultaneous reactions, namely :

(a) the bimolecular reaction :



(b) the trimolecular reaction :

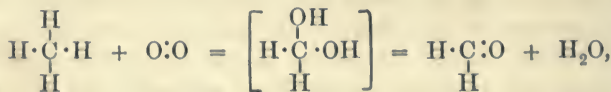


possibly the latter may involve the formation and very rapid decomposition of formic acid, thus :



For the present, it must remain a matter of conjecture as to whether the precise mechanism of the primary oxidation to formaldehyde and steam is better represented by the foregoing equations or by assuming

the formation and rapid decomposition of the hypothetical  $\begin{array}{c} \text{OH} \\ | \\ \text{H} \cdot \text{C} \cdot \text{OH} \\ | \\ \text{H} \end{array}$ , thus :



both atoms of the oxygen molecule actually entering that of the hydrocarbon before the elimination of steam occurs.

It may be remarked that the foregoing views not only accord with and explain all the facts observed in the case of methane, but are also entirely confirmed by the results of experiments on ethane.

#### EXPERIMENTAL.

##### A. An Apparatus for the Investigation of Slow Combustion Processes.\*

The apparatus we have devised for these and other similar experiments is shown in the accompanying diagram (Fig. 1, p. 1077). It is

\* Two examples of the circulation apparatus have been installed in our laboratory for these experiments, and the present description will suffice for reference in any

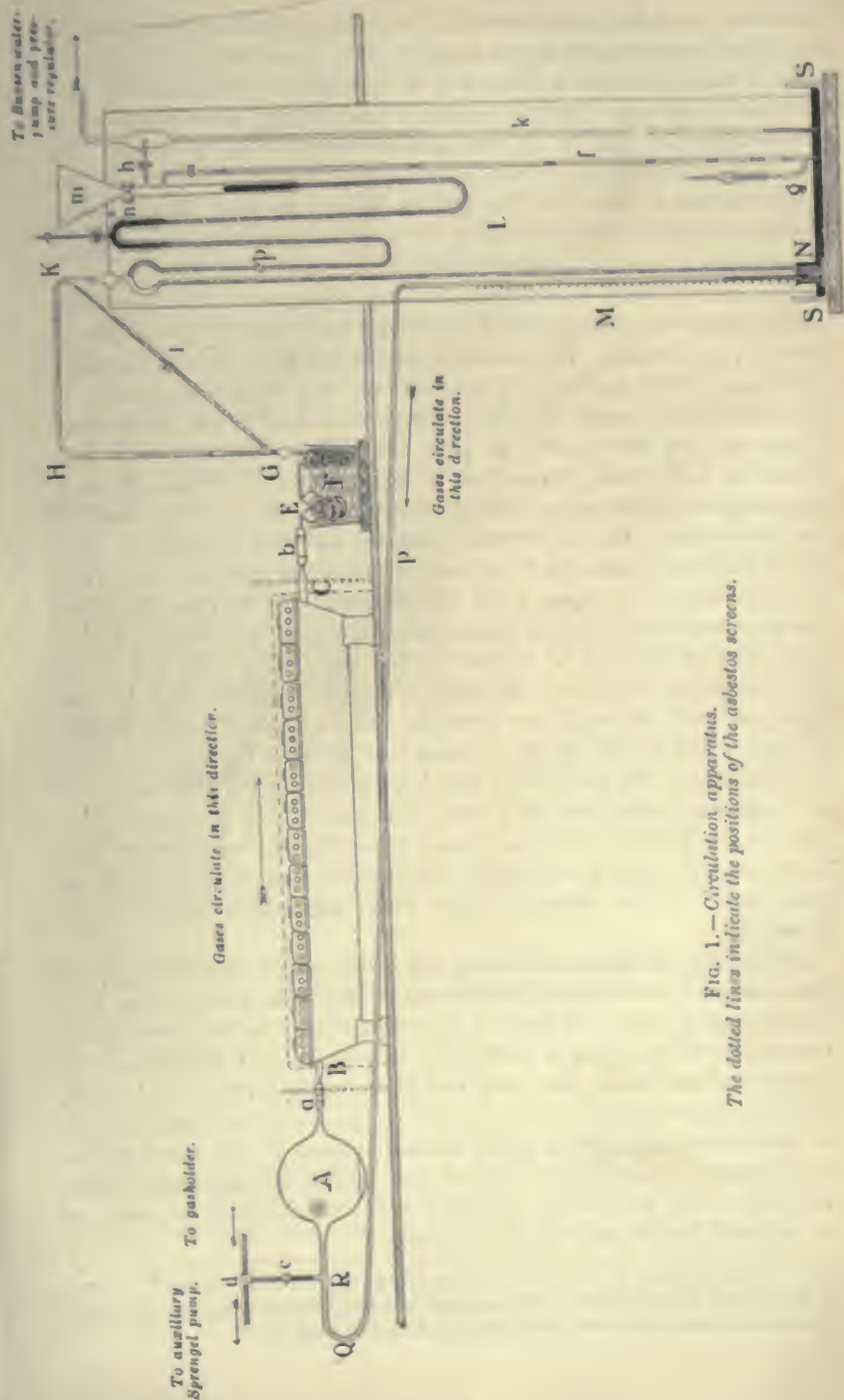


FIG. 1.—Circulation apparatus.  
The dotted lines indicate the positions of the asbestos screens.

essentially a closed system in which the reacting gaseous mixture can be circulated continuously day and night, at a practically uniform rate, over a heated surface (maintained at a constant temperature), and afterwards through suitable washing and cooling arrangements for the removal of soluble or condensable intermediate products. By means of a manometric arrangement, the pressure of the gas in the apparatus can be recorded at regular intervals, so that, given regular working conditions, the velocity of a given reaction, or group of simultaneous reactions, can be measured.

The more detailed description of the various parts of the apparatus will perhaps be made clearer if we follow the course of the gas round the complete circuit. The starting point is the glass globe *A* (capacity 1200 c.c.), which serves as a reservoir for the circulating gases; in the actual experiments, the globe always contained a few cubic centimetres of distilled water, so that the gaseous mixture was kept saturated with water vapour at a temperature  $t^{\circ}$ , indicated by a thermometer placed against the globe with its bulb actually touching the outer wall. The globe was carefully screened by asbestos cardboard both from radiation from other parts of the apparatus, and from draughts caused by open doors or windows. On leaving the globe, the gases traversed the Jena glass combustion tube, *BC* (length 75 cm.), filled with fragments of ignited porous porcelain; each end of the tube was drawn out to the diameter of ordinary quill tubing in such a manner that the narrower portions project several inches beyond the bed of the Lothar Meyer constant temperature furnace on which the tube rests. The two joints, *a* and *b*, connecting *BC* with the rest of the apparatus were made with very stout indiarubber pressure tubing, the two glass ends underneath being gradually pushed together until they actually came into contact; with these two exceptions, all the other joints in the apparatus were fused together by means of the blowpipe.

On leaving the combustion tube, the gases passed first through the glass worm, *E*, containing distilled water, and then through the long glass spiral, *F*. Both *E* and *F* were surrounded by a water-jacket, through which a stream of cold water was maintained throughout the experiment in order to ensure the rapid cooling of the hot gases. Since the mixture entered the combustion tube saturated with moisture at the ordinary temperature, any steam produced by the interaction of the gases, as well as any soluble or condensable intermediate product which survived the passage over the heated surface, would be condensed or absorbed in this part of the apparatus.

In future communication we may make on the subject of "slow combustion." It may be added that the apparatus is well adapted for the determination of the velocity of gaseous reactions, and is now being employed for this purpose.



The cooled gases passed onwards to the automatic Sprengel pump, *L*, through the triangular arrangement *GHK*, the object of which will be explained later. The pump delivered the gases into the vertical manometric tube *M*, standing over mercury in the vessel *N*; thence they passed forward through the horizontal tube *P*, round the curve *Q*, past the T-piece *R*, back into the globe *A*, thus completing the circuit. A millimetre scale placed behind the manometer *M* enabled the pressure of the moist gases to be read at regular intervals, the automatic Sprengel pump being thrown out of action for a moment by shutting the tap *p*.

The apparatus was closed by the glass tap *c*, working in a mercury cup and sealed into the vertical branch of the T-piece *R*. On the other side of *c* was sealed the glass T-tap *d*, through which communication could be made either with (1) the glass gas-holder containing the mixture to be investigated, or (2) an auxiliary Sprengel pump (not shown in the diagram). This latter was used either during the preliminary exhaustion of the apparatus or (if necessary) for the removal of samples of gases during the course of an experiment. All the joints between this auxiliary pump or the gas-holder and the tap *c* were fused by means of the blowpipe.

As it was necessary, for the complete success of an experiment, to ensure a continuous circulation of the gases in the apparatus at a uniform rate by day and night, for, if need be, many days together, special arrangements had to be made for working the automatic Sprengel pump under constant conditions throughout. For a long time, this constituted a serious experimental difficulty, but happily it was finally entirely overcome. We may briefly indicate the general character of these arrangements.

The automatic working of the Sprengel pump was secured by means of a Bunsen water-pump, the suction of which was kept constant by inserting an automatic pressure regulator (the action of which depended on the making and breaking of a mercury seal within narrow limits of pressure) between the two pumps; to this regulator was attached a large glass bottle of some 20 litres capacity, the effect of which was to keep the suction perfectly steady. The suction of the water-pump raised the mercury from the glass trough *SS* up the vertical tube *f* to a height a little above the junction with the side piece *g*, which had a capillary termination. Minute quantities of air drawn in through this capillary broke the column of mercury in *F* into short threads and drove them to the head of the pump. In the event of the mercury being drawn up *F* faster than it fell down the fall-tube of the pump, the excess overflowed through the horizontal branch *h* into the vertical tube *k*, which also indicated the suction of the water-pump. At the outset of an experiment, it was occasionally

necessary to start the Sprengel pump by a head of mercury in the funnel *m*; in a few minutes, however, this was cut off by the tap *n* and the automatic working started. The glass tap *p* served to adjust the rate of fall of the mercury in the fall-tube and to throw the pump momentarily out of action whenever the pressure of the gas in the apparatus was read.

It will be readily understood that a continuous circulation could only be maintained with an automatic Sprengel of this type so long as the pressure of the gas at the top of the fall-tube kept below a certain limit, in this particular case about 600 mm. In order that we might have higher pressures than this in the main apparatus, and still ensure continuous and satisfactory working, we adopted a device represented by the triangle *GHIK*. Into each of the sides *GHI*, *HK*, was sealed a length of very fine capillary tubing, whilst a perfectly free passage was allowed through the base *GK*. By closing the tap *e*, the circulating gases were compelled to pass through the capillaries, so that, although the pressure in the main apparatus might be nearly atmospheric, a low pressure could be maintained between *K* and the top of the fall-tube of the automatic Sprengel pump. By opening *e*, the capillaries could be thrown out of circuit and the gases allowed a free passage through *GK*.

The total capacity of the apparatus was about 1450 to 1500 c.c., and when filled under 600 mm. pressure it contained 1150 to 1200 c.c. of the mixture under examination (measured under atmospheric pressure). It may be understood that the speed at which the mixtures were circulated, although constant throughout a given experiment, varied in different experiments and was such that the whole gaseous mixture would complete a circuit once in 1 or 2 hours, each portion of the gases probably remaining about 3 to 6 minutes in the combustion tube during each cycle; these times represent, approximately, the maximum and minimum speeds respectively.

*Method of Conducting an Experiment.*—At the outset of an experiment, the apparatus was thoroughly exhausted, the tube *BC* being heated to between 250° and 300° in order to expel all air enclosed in the pores of the porcelain it contained. All permanent gas having thus been withdrawn from the apparatus, the pumps were stopped, the furnace turned out, and the whole allowed to remain for at least 12 hours in order to test the tightness of taps and the two joints *a* and *b*.

The gaseous mixture under investigation was then slowly admitted into the apparatus from the holder until the desired pressure (usually a little over 600 mm.) was attained. The tap *C* was then closed and the mixture circulated in the cold for 12 hours in order that it might become thoroughly saturated with water vapour at the temperature (*t*°) of the room, and that all adjustments necessary for the regular and



continuous working of the automatic Sprengel pump might be made. A sample of the mixture was then withdrawn for analysis through the auxiliary Sprengel pump, after which the pressure of the cold moist gas, at the room temperature ( $t^\circ$ ), was finally taken. The furnace was lighted and covered by an asbestos screen (indicated by dotted lines in the diagram); the gas supply of the furnace passed through a Stott's governor, and a practically constant temperature ( $T^\circ$ ) in the combustion tube could be maintained throughout an experiment. As soon as the furnace had acquired the desired maximum temperature ( $T^\circ$ ), which was recorded by a Geissler mercurial thermometer filled with nitrogen under pressure and graduated up to  $550^\circ$ , all the screens were finally adjusted in position and the pressure of the moist gas in the apparatus again determined. The experiment was then allowed to run its course through many consecutive days, pressure and temperature records being taken at regular intervals until it was thought that the reaction had gone far enough. Finally, the furnace was turned out, the screens removed, and the whole apparatus allowed to cool down during several hours to the room temperature. The pressure of the cold moist gas was again determined, samples of the gaseous product being subsequently withdrawn for analysis through the auxiliary Sprengel pump. Lastly, the worm *E* and spiral *F* were removed and the contents examined.

### B. Details of Experiments.

The methane was prepared by the action of an aluminium mercury couple on a solution of methyl iodide in methyl alcohol, and purified according to the method described in our previous paper (*loc. cit.*, p. 541); great care was taken to ensure the complete removal of last traces of free hydrogen by repeatedly passing the gas over oxidised palladium sponge at  $100^\circ$ .

The oxygen was obtained by heating potassium permanganate in small glass bulbs; it was washed through strong caustic potash solution. The mixtures were made in graduated glass holders over strong sulphuric acid.

*1st Experiment.*—This extended over 24 consecutive days, during which the furnace temperature only varied between  $450^\circ$  and  $455^\circ$ . Leaving out of the reckoning a small percentage of nitrogen, the original mixture had the percentage composition: \* methane, 66.45; oxygen, 33.55.

\* In order to make all measurements in the various experiments strictly comparable we propose, throughout this paper, as in our last communication, to express the compositions of the various gaseous mixtures, and also all pressure records, in terms of the 'nitrogen free' gases. Since in analysing the gases the nitrogen



The speed of circulation was slow, the capillaries in the triangle *GHK* being in circuit the whole time. The daily records showed a continuous fall of pressure in the reacting gases, but owing to small variations in the rate of circulation (this was the first experiment made with the apparatus) the daily fall of pressure was not quite so regular as in the subsequent experiment. However, during a period of several days, any small variations in the speed of circulation ceased to affect the general result, and the pressure falls over successive intervals of 2 or 3 days were quite regular. We need only record the corrected pressures for the dry 'nitrogen free' gas at the outset of the experiment, and at the end of 8, 16, and 24 days respectively.

| Time in days from commencement. | Pressure of dry 'nitrogen free' gas at 0° in mm. | Corrected pressure fall in mm. | Percentage pressure fall. |
|---------------------------------|--|--------------------------------|---------------------------|
| 0                               | 591.4  | 54.8                           | 9.25                      |
| 8                               | 536.6  |                                |                           |
| 16                              | 490.0  | 46.6                           | 7.90                      |
| 24                              | 452.0  | 38.0                           | 6.45                      |
|                                 |  | Totals 139.4                   | 23.60                     |

The residual 'nitrogen free' gases, analysed according to the method described in our previous paper (*loc. cit.*, p. 545), had the following percentage composition :

|                       |      |               |        |
|-----------------------|------|---------------|--------|
| Carbon monoxide ..... | 4.46 | Methane ..... | 70.40  |
| Carbon dioxide .....  | 9.84 | Oxygen .....  | 15.30  |
|                       |      |               | 100.00 |

The ratio  $C/A$ , determined by exploding the residual gas, after removal of the oxygen and the oxides of carbon with excess of oxygen and air, was exactly 2.00, proving the entire absence of free hydrogen in the products.

The presence of so large a proportion of carbon dioxide in the products is partly due to the circumstance that carbon monoxide and moist oxygen react under the experimental conditions (see footnote, p. 1085).

We may now examine how far these gaseous products account for the methane and oxygen originally introduced into the apparatus; this may best be done by comparing the partial pressures of the methane and oxygen in the original mixture with the partial pressures

was in each case determined "by difference," after all other constituents had been estimated, the numbers for the percentage compositions of our 'nitrogen free' gas will always add up to 100 exactly.

of the various gaseous products at the end of the experiment, as follows :

Partial pressures of methane and oxygen in original mixture.

|         | mm.              |   | mm.    |
|---------|------------------|---|--------|
| Methane | = 591.4 × 0.6645 | = | 393.1. |
| Oxygen  | = 591.4 × 0.3355 | = | 198.3. |

| Partial pressures of the products. | mm.            | Corresponding with mm. of the original |              |
|------------------------------------|----------------|--|--------------|
|                                    |                | Methane                                | Oxygen       |
| CO = 452 × 0.0446                  | = 20.15 .....  | 20.15 .....                            | 30.20        |
| CO <sub>2</sub> = 452 × 0.0984     | = 44.45 .....  | 44.45 .....                            | 88.90        |
| CH <sub>4</sub> = 452 × 0.7040     | = 318.20 ..... | 318.20 .....                           | —            |
| O <sub>2</sub> = 452 × 0.1530      | = 69.20 .....  | —                                      | 69.20        |
|                                    |                | <hr/> 382.80                           | <hr/> 188.30 |

Hence, of the methane (393.1 mm.) and oxygen (198.3 mm.) originally introduced into the apparatus, only 382.8 mm. of methane and 188.3 mm. of oxygen respectively are accounted for in the gaseous products. The natural inference is, therefore, that practically equal volumes (CH<sub>4</sub> = 10.33 mm., O = 10 mm.) had reacted to form some soluble or condensable intermediate product. This first led us to suspect the formation of formaldehyde by the interaction of equal volumes of the original gases, thus, CH<sub>4</sub> + O<sub>2</sub> = CH<sub>2</sub>O + H<sub>2</sub>O.

The liquid in the worm *E* at the end of the experiment was neutral to litmus, but on testing it with a solution of rosaniline hydrochloride previously decolorised by sulphurous acid a very pronounced aldehyde reaction was obtained. Hence, we may conclude that of the 75 mm. of original methane which the foregoing numbers show had been oxidised during the experiment, 10 mm., or over 13 per cent., were accounted for as formaldehyde.

*2nd Experiment.*—This was perhaps the best we have made with methane and oxygen; it extended over 10 days, during which time the rate of circulation was practically constant throughout.\* At the end of the experiment, nearly the whole of the original oxygen had disappeared.

The original mixture contained some 0.8 per cent. of nitrogen, but leaving this out of the reckoning its percentage composition was methane, 66.5; oxygen, 33.5.

The pressure of the cold dry 'nitrogen free' mixture charged into the circulation apparatus was 513 mm. at 16°. After ascertaining

\* The rate of circulation in this experiment was approximately twice as great as that maintained during the first experiment; the temperature of the combustion tube was also higher. These two circumstances account for the more rapid oxidation observed in the second experiment.

this pressure, the furnace was lighted and the temperature of the combustion tube raised during the first 3 or 4 hours to  $460^{\circ}$ , and afterwards to just above  $500^{\circ}$ ; during the remainder of the experiment, the furnace temperature only varied between  $497^{\circ}$  and  $510^{\circ}$ .

The following were the daily records taken :

| Day. | Temperature of<br>combustion tube,<br>$T^{\circ}$ . | Temperature of gas<br>in globe <i>A</i> .<br>$t^{\circ}$ . | Corrected pressure of<br>dry 'nitrogen free'<br>gas at $22^{\circ}$ ,<br>mm. |
|------|---|--|--|
| 0    | 460°  | 22.0°  | 554.7  |
| 1    | 510   | 24.5   | 482.3  |
| 2    | 510   | 22.3   | 462.8  |
| 3    | 510   | 22.0   | 439.7  |
| 4    | 505   | 23.0   | 424.0  |
| 5    | 498   | 23.5   | 411.7  |
| 6    | 498   | 24.5   | 395.3  |
| 7    | 498   | 25.7   | 384.9  |
| 8    | 497   | 22.8   | 375.7  |
| 9    | 497   | 22.0   | 367.0  |
| 10   | 498   | 24.2   | 350.0  |

The pressure curve (ordinates = pressures, abscissæ = time in days) for this experiment (Fig. 2, p. 1085) shows how regularly and continuously the pressure diminished throughout; the proportionately larger falls observed during the first and tenth days, respectively, are to be attributed to a slight acceleration in the rate at which the gases were circulated over the heated surface.

The pressure of the cold dry 'nitrogen free' products after the furnace had been put out and the apparatus allowed to cool down to the room temperature was 335.9 mm. at  $16^{\circ}$ . Hence, the total diminution of pressure of the cold dry gas, at  $16^{\circ}$ , during the experiment was  $(513 - 335.9) = 177.1$  mm. or 34.5 per cent. This alone is sufficient to prove the formation of some condensable or soluble intermediate product, for had the whole of the oxygen originally present reacted with methane to form  $\text{CO}_2$  and steam (and the analysis of the product indicated that a portion of the original oxygen remained over), the diminution of pressure would only have been 33.5 per cent.

Three very concordant analyses of the gaseous products showed that the 'nitrogen free' gas contained :

|                       |       |               |       |
|-----------------------|-------|---------------|-------|
| Carbon monoxide ..... | 0.50  | Oxygen .....  | 4.15  |
| Carbon dioxide .....  | 19.85 | Methane ..... | 75.50 |

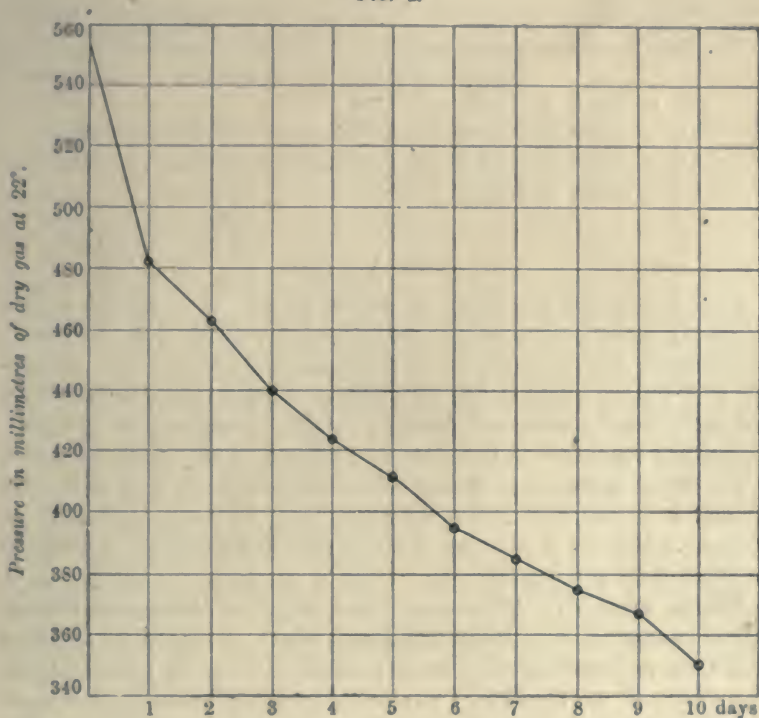
100.00

The ratio  $C/A$ , found by exploding the residual gas, after removal of  $\text{CO}_2$ ,  $\text{CO}$ , and oxygen with excess of oxygen and air, was 1.992,



again proving the entire absence of free hydrogen in the products. In this instance, also, it should be pointed out that the extremely large ratio,  $\text{CO}_2/\text{CO}$ , in the gaseous products is largely due to the fact that carbon monoxide and oxygen combine quite readily at  $500^\circ$  under the experimental conditions.\*

FIG. 2.



Curve showing daily pressure fall in the mixture  $2\text{CH}_4 + \text{O}_2$  when circulated over a surface maintained at  $500^\circ$  (second experiment).

Comparing now, as in the case of the first experiment, the partial pressures of the original mixture, as introduced into the apparatus,

\* That this is so we have proved directly by examining moist mixtures of carbon monoxide (2 vols.) and oxygen (1 vol.) in the circulation apparatus, the temperature of the combustion tube being kept constant at  $450^\circ$ , and any carbon dioxide being absorbed as fast as it was produced by a suitable absorbent in the worm *E*. In one experiment, nearly 80 per cent. of the mixture combined in eight days. We are now investigating the velocity of the reaction with a view to determining its order and character. The curves obtained indicate that the velocity is nearly proportional to the pressure of the reacting mixture. We hope before long to communicate the details of these experiments.

with those of the final gaseous products, we obtain the following numbers:

Partial pressures for original mixture (nitrogen free).

Methane =  $513 \times 0.665 = 341.1$  mm.

Oxygen =  $513 \times 0.335 = 171.9$  „

| Partial pressures of gaseous products.    | mm.         | Corresponding with mm. of<br>the original |             |
|---|-------------|---|-------------|
|   |             | Methane.                                  | Oxygen.     |
| CO = $335.9 \times 0.005 =$               | 1.7 .....   | 1.7 .....                                 | 2.5         |
| CO <sub>2</sub> = $335.9 \times 0.1985 =$ | 66.6 .....  | 66.6 .....                                | 133.2       |
| O <sub>2</sub> = $335.9 \times 0.0415 =$  | 14.0 .....  | — .....                                   | 14.0        |
| CH <sub>4</sub> = $335.9 \times 0.7550 =$ | 253.6 ..... | 253.6 .....                               | —           |
|   |             | <hr/> 321.9                               | <hr/> 149.7 |

Thus, out of the 341.1 mm. of methane and 171.9 mm. of oxygen originally introduced into the apparatus, only 321.9 and 149.7 mm., respectively, are accounted for in the gaseous products. The remaining 19.2 mm. of methane and 22.2 mm. of oxygen (again nearly equal volumes) must have reacted forming soluble 'intermediate' products. This would represent no less than 22 per cent. of the methane burnt.

The liquid in the worm *E* was found to be distinctly acid to litmus; it had a pronounced aldehydic smell, and instantly restored the magenta colour to a solution of rosaniline hydrochloride previously decolorised by sulphurous acid. With a solution of *p*-bromophenylhydrazine acetate in dilute acetic acid, it gave an immediate canary-yellow precipitate of a bromohydrazone, which proved to be identical with that prepared directly from a dilute solution of formaldehyde. The acidity of the liquid may be attributed to the presence of a small quantity of formic acid, the formation of which would also explain why rather more of the oxygen than of the methane of the original mixture was unaccounted for in the gaseous products (see previous paragraph). We cannot say definitely whether the formic acid was due to the further oxidation of formaldehyde vapour in the heated tube or of liquid formaldehyde in the worm. It may, however, be pointed out that no formic acid was produced in the first experiment, where the rate of circulation was much slower,\* and that in neither experiment could we detect any formation of methyl alcohol. The proportionately larger amount of formaldehyde found in the second experiment (22 per cent. of the methane oxidised, as compared with

\* This fact favours the view that the formic acid detected in the second experiment originated in the hot combustion tube.

only 13 per cent. in the first experiment) is undoubtedly due to the more rapid rate at which the reacting gases were circulated over the heated surface, and afterwards through the water in the worm and spiral.

Other similar experiments with methane and oxygen have been made at various times, but since the results are identical with the foregoing, they need not be further described. In no case was there any sign of a deposition of carbon or liberation of free hydrogen, and they were all characterised by a continuous and regular diminution of pressure, and by the formation of formaldehyde.

It was just possible that this formaldehyde might have been produced by the rapid combination of carbon monoxide and free hydrogen liberated in a primary reaction of the following type:  $\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2 + \text{H}_2\text{O}$ , followed by  $\text{CO} + \text{H}_2 = \text{CH}_2\text{O}$ . This, of course, could only be the case did carbon monoxide and hydrogen combine with a velocity infinitely great as compared with the oxidation velocity of methane or of formaldehyde, since no free hydrogen was ever found in the final products. We therefore circulated a mixture of equal volumes of carbon monoxide and hydrogen in the apparatus for 2 days, the furnace being maintained at temperatures ranging between  $460^\circ$  and  $480^\circ$ . The results were entirely negative; no change in the pressure of the mixture was observed, and not a trace of formaldehyde was produced. Hence the view of the formation of formaldehyde just indicated is inadmissible.

These experiments are being extended to other hydrocarbons (ethane, propane, ethylene, acetylene, &c.) in the hope that by a thoroughly systematic examination of typical cases, sufficient data may in time be accumulated to justify a general theory of the mechanism of the oxidation of hydrocarbons.

In conclusion, we desire to express our indebtedness to the Government Grant Committee of the Royal Society for grants, which have materially helped us to meet the expenses of these researches.

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CVI.—*The Mechanism of Combustion.*

By HENRY E. ARMSTRONG.

THE proof given by Dr. Bone and Mr. Wheeler that formaldehyde is a product of the interaction of moist gaseous oxygen and methane, consequently, that the process of combustion is of the same nature in the gaseous as in the liquid state when complex oxidising agents are used, appears to be of crucial importance. It affords the opportunity which I have long awaited of effectively considering the arguments advanced by Prof. H. B. Dixon in his paper on "The mode of formation of carbonic acid in the burning of carbon compounds" (*Trans.*, 1896, 69, 774)—in which views expressed by me at various times\* on the subject were referred to and more or less traversed—and of formulating a series of propositions of general application to combustion and similar phenomena.

If Dixon, in the paper referred to, does not display disbelief in what may be termed an electrolytic explanation of the phenomena, he at least has difficulty in understanding the nature of the process and its exact application. This is shown, for example, by the manner in which he refers (on p. 777) to the possibility of some interactions occurring independently of electrolytic action.

It seems to me to be necessary to regard all the phenomena from one point of view and to assume that chemical interchange and electrolysis are interchangeable equivalent terms. Looked at in this manner, oxidation is an indirect process, inasmuch as the oxygen used is only indirectly incorporated with the oxidised material, the oxidation taking place in a circuit composed of the oxidisable substance, *conducting water*† and oxygen, this last playing the part of depolariser—for example, in the manner depicted broadly in the equation:



The view put forward by Traube that hydrogen peroxide is invariably a product of such interactions finds expression in this equation. Besides being supported by a large amount of experimental evidence, this hypothesis has much to recommend it as a rational explanation,

\* *Proceedings*, 1885, 39; 1892, 22. *Trans.*, 1886, 49, 112; 1895, 67, 1122. *Proc. Roy. Soc., Brit. Assoc. Report*, 1885, 962; 1886, 40, 287; 1902, 70, 99. *Nature*, 1893, 49, 100.

† It must not be forgotten that water alone cannot act as the electrolyte; it is to be supposed, especially in view of the crucial observations made by H. B. Baker (*Trans.*, 1902, 30, 400. Compare *Proc. Roy. Soc.*, 1902, 70, 99), that a composite electrolyte is always formed by the association of [the water with another pseudo-dielectric (usually present as an impurity)].

especially as it reduces the number of molecules required for an effective conjunction, thus diminishing a difficulty on which Dixon has dwelt (*loc. cit.*, p. 777).

It is scarcely necessary to point out what would be the fate of hydrogen peroxide if formed in the manner supposed: in part, at least, it would undergo decomposition by heat but it might also act in part as depolariser :



Mendeléeff has already called attention to the fact that when regarded from the above point of view, the formation of water is an oscillatory process.\*

Even in the case of the combustion of hydrogen, it is open to question whether the molecule undergoes oxidation directly or whether the process is one of hydroxylation: whether oxygen is directly added to the molecule or not. In the latter case, the process may be represented somewhat as follows :



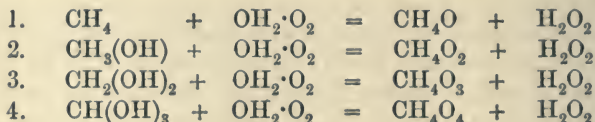
The answer given to such a question must depend on the view taken as to the manner in which water is affected on electrolysis; much is to be said in favour of the hydroxylation hypothesis: I prefer it.

Whatever be the precise nature of the oxidation process, however, in view of Bone and Wheeler's observations, it may be supposed that the hydrocarbon molecule is oxidised in a series of independent consecutive operations, neither hydrogen nor carbon being burnt preferentially, in which the oxygen is gradually introduced into the molecule and distributed between the carbon and hydrogen (compare *Proc.*, 1892, 8, 22).

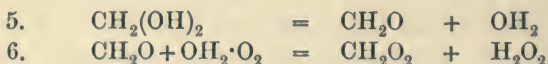
\* This opinion [that in the combustion of hydrogen with oxygen, hydrogen peroxide is first formed, which is decomposed by the heat evolved into water or oxygen, which I have always held since the first edition of this work] as to the primary origin of hydrogen peroxide and of the formation of water by means of its decomposition has recently been more generally accepted, thanks more especially to the work of Traube. Probably it explains most simply the necessity for the presence of traces of water in many reactions, as, for instance, in the explosion of carbonic oxide with oxygen, and perhaps the theory of the explosion of detonating gas itself and of the combustion of hydrogen will gain in clearness and truth if the preliminary formation of hydrogen peroxide and its decomposition be taken into consideration. I may here point out the fact that Ettingen (at Dorpat, 1888) observed the existence of currents and waves in the explosion of detonating gas by taking photographs which showed periods of combustion and the waves of explosion which should be taken into consideration in the theory of this subject (*Principles of Chemistry*, 2nd English edition, 1, 312).

But inasmuch as changes take place under the influence of the heat developed, whereby the more or less immediate products of oxidation are decomposed, products may come into existence which are only indirectly related to the substance originally attacked. To quote Sir G. G. Stokes, "We must carefully distinguish between the changes which take place in the partial combustion of a molecule and those which are produced in neighbouring molecules as a result of the heat thus produced." Otherwise stated, we have to distinguish between exothermic and endothermic changes.

In the case of methane, the following primary changes probably all take place as the oxidation of the molecule proceeds :



It is not to be supposed that oxidation is effected entirely in accordance with this scheme. The formaldehydol, produced at stage 2, in some, if not in large, part, is perhaps at once resolved into water and formaldehyde; the latter then undergoes conversion into formic acid :



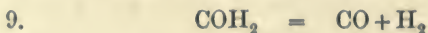
The same argument applies with greater force to the formacid-hydrol produced at stage 3; perhaps the greater part of the carbonic acid is produced by the oxidation of formic acid :



The production of carbon monoxide may be ascribed, at least in large part, to the occurrence of the simple heat change :



But it is conceivable that carbon monoxide may also be formed in part by the decomposition of formaldehyde :



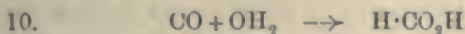
Whether and to what extent and under what conditions both of these changes take place, experiment alone can decide.

Whichever view be taken, carbon monoxide is a secondary product, not a direct product of the oxidation of the hydrocarbon nor of any preferential oxidation of the carbon.

If the oxidation of carbon monoxide, whether by means of moist

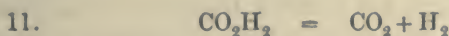


oxygen or of steam alone, be pictured as involving the prior formation of formic acid, it is possible to explain the fact that the combustion of carbon monoxide is so much dependent on the presence of a considerable proportion of water molecules; at elevated temperatures, change would proceed only very partially in the direction:

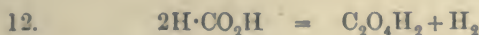


consequently a considerable preponderance of water molecules would be required to favour change in this direction. I think this argument must now outweigh that put forward by Dixon in 1886 (*Trans.*, 49, 106).

Assuming, however, that formic acid is produced by the interaction of carbon monoxide and steam, it is open to question whether the carbon dioxide and hydrogen which are the ultimate products of change at high temperatures are produced simply by the decomposition of the formic acid:



or whether, bearing in mind the readiness with which formates yield oxalates, oxalic acid and hydrogen are not formed at an intermediate stage:

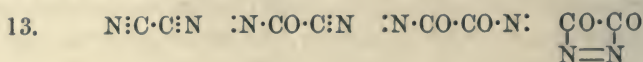


We need to use methods such as Deville and Dewar have introduced of studying dissociation phenomena at high temperatures to solve problems such as these.

Bone and Wheeler are apparently inclined to regard formaldehyde as an initial product of change produced by the incorporation of a single molecule of oxygen into the methane molecule. Not only is this interpretation open to question from the point of view here taken as to the nature of the primary process of oxidation; it is, perhaps, also open to question because it involves the assumption that the molecule is, as it were, attackable from two sides at once. The discussion of this issue will be of importance at some future date; I refer to it now mainly in order that the importance may be apparent of experiments devised to test whether methyl alcohol be not discoverable among the products of the gradual oxidation of methane.

Dixon has specially called attention to the behaviour on combustion of cyanogen. As he has shown, this burns preferably to carbon monoxide, although if sufficient oxygen be present it burns to carbon dioxide. It would seem now to be no more difficult to interpret the behaviour of this gas than that of hydrocarbons. The combustion

may be assumed to take place gradually, more or less in a manner to give rise to a *series of oxidation products* such as the following :

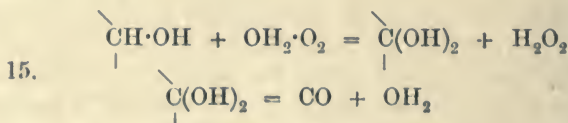


In the absence of oxygen, the cycloid thus formed decomposes (explodes) into nitrogen and carbon monoxide ; but if oxygen be present in excess, it is either directly oxidised or—which is perhaps more probable—the carbon monoxide formed by its decomposition undergoes oxidation in the nascent state. It is to be supposed that moisture must be present but that a very minute proportion suffices, cyanogen being far more sensitive to attack than carbon monoxide.

The action of steam, as well as of moist oxygen, on carbon and the preferential formation of carbon monoxide by the combustion of carbon may be explained from a similar point of view. The carbon molecule is undoubtedly a complex structure, probably of the benzenoid type (compare *Encyc. Brit. Sup.*, vol. II, 732). It appears probable that when subjected to the action of water at a high temperature, each element of the complex sooner or later associates itself with a water molecule ; the compound thus formed subsequently breaks up into carbon monoxide and hydrogen :



In presence of oxygen, the action proceeds a stage further, giving rise to a compound which breaks down into carbon monoxide and water :



In the case of complex carbon compounds generally, there can be little doubt that products of oxidation formed at an early stage break down into simpler incompletely oxidised products, which undergo oxidation independently. It is probable that the formation of unsaturated hydrocarbons and even of carbon is often brought about in this manner. For example, ethylene, in presence of a limited proportion of oxygen, might initially be converted into hydroxyethylene and this might be at once resolved into acetylene and water. Acetylene, in like manner, might give rise to hydroxyacetylene and this to carbon and water.

No doubt, under certain conditions, hydrocarbons may undergo simple heat changes, as when heated alone ; so long as oxygen is

present, however, these changes probably take place to a subordinate extent.

There is little reason to suppose that changes take place at high temperatures, in rapid combustions, in ways very different from those in which they occur at lower temperatures, although certain changes will undoubtedly take place to a greater extent under the one set of conditions than under the other.

The effective operation is not the mere blow due to impact or the vibration caused by this in the molecule, but the conjunction of compatible molecules and the consequent formation of composite systems within which change can occur. In so far as temperature influences the formation of compatible systems, either as regards their character or the rate at which they arise, temperature has an influence—but probably not otherwise.

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### CVII.—*The Constituents of the Volatile Oil of the Bark of Cinnamomum pedatinervium, of Fiji.*

By ERNEST GOULDING, D.Sc., Lond.

THE bark of *Cinnamomum pedatinervium*, a tree indigenous to the Fiji Islands, possesses a pleasant, aromatic, spicy odour, due to the secretion of a volatile oil. The following account is given by Berthold Seemann in his "Flora Vitiensis" (p. 202).

"The bark of the 'Macou,' as it is termed in the Bau dialect, 'Mou' in that of Kadavu, and 'Maiu' in that of Namosi, is a kind of Cassia bark, which may prove of commercial importance, and is used by the Fijians for scenting cocoa-nut oil. The tree yielding it is about thirty feet high, four to five inches in diameter, and is met with above an elevation of 1500 feet, in dense virgin forests. I found it on Buke Levu, island of Kadavu, and on Vona peak, Viti Levu; and Mr. Pritchard received fine specimens from the islands of Gau, where they had been collected by W. Berwick, a coloured man, residing there. The bark has a fine aromatic smell and flavour, a light brown colour, is thicker than that of the cinnamon of commerce, and resembles some of the laurineous barks, such as the Sintoc and Culilawang, brought from the Moluccas. In Namosi, it is used as a sudorific. Unfortunately, I did not see the tree in flower, and hence am unable to determine whether the 'buds' are equal to the best 'Cassia buds' of commerce. The resemblance of the Fijian names to that of 'Massoy,' given to a fine quality of Cassia bark, from New Guinea, deserves investigation."



A sample of this bark having been sent from Suva, Fiji, to the Imperial Institute in order that its volatile oil might be submitted to examination and commercial valuation, the investigation described in the following pages was carried out in the Laboratories of the Scientific and Technical Department of the Institute.

### EXPERIMENTAL.

A quantity of the powdered bark weighing  $50\frac{1}{2}$  lbs., on distillation with steam, yielded  $7\frac{1}{2}$  oz. of the volatile oil, which is equivalent to 0.92 per cent. The oil is almost colourless when first distilled, but gradually assumes a yellowish-brown colour. It has a sweet, aromatic odour and a pungent, spicy taste. It has a rotatory power of  $-4.78^\circ$  at  $15^\circ$  in a 100 mm. tube, or  $[\alpha]_D -4.96^\circ$ ; when, however, the oil is heated to  $170^\circ$  and allowed to cool again, the rotatory power is increased to  $-5.48^\circ$  or  $[\alpha]_D -5.66^\circ$ . Its index of refraction is 1.4963 at  $15^\circ$ . It is freely soluble in the usual organic solvents, and is neutral to litmus. When the oil is cooled to  $-12^\circ$  for an hour in a mixture of ice and salt, no solid substance separates.

The oil was distilled under atmospheric pressure, and the following fractions were obtained:  $180-205^\circ$ , 22 per cent.;  $205-220^\circ$ , 30 per cent.;  $220-230^\circ$ , 27 per cent.;  $230-255^\circ$ , 18 per cent.; the residue in the distilling flask amounted to 3 per cent. and was of a dark brown colour. The physical characters of the oil and these fractions are given in the following table. The optical rotatory power was in each case determined in a 100 mm. tube by means of a Laurent's half-shadow polarimeter. The refractive indices were determined in a hollow glass prism by means of the spectrometer.

|                 | Boiling at      | Specific gravity<br>$15^\circ/15^\circ$ . | $[\alpha]_D$ . | $n_D$ . |
|-----------------|-----------------|---|----------------|---------|
| Oil .....       | —               | 0.964                                     | $-4.96^\circ$  | 1.4963  |
| Fraction I..... | $180-205^\circ$ | 0.915                                     | $-11.37$       | 1.4816  |
| „ II.....       | $205-220$       | 0.953                                     | $-6.69$        | 1.4918  |
| „ III.....      | $220-230$       | 0.993                                     | $-2.40$        | 1.5068  |
| „ IV.....       | $230-255$       | 1.013                                     | $-1.91$        | 1.5161  |

### *Estimation of Esters.*

A quantity of the oil weighing 3.1810 grams was boiled with  $N/2$  alcoholic potassium hydroxide for half an hour. After the solution had cooled, it was titrated with  $N/2$  hydrochloric acid, phenolphthalein being employed as the indicator. It was found that 0.5 c.c. of the

alkali had been neutralised, equivalent to a saponification number 4.4, whence the percentage of esters in the oil amounts to 1.5 per cent. (calculated as  $C_{10}H_{17} \cdot C_2H_3O_2$ ).

#### *Estimation of Alcohols.*

A mixture of 5 c.c. of the oil, 10 c.c. of acetic anhydride, and 1 gram of anhydrous sodium acetate was boiled for  $1\frac{1}{2}$  hours in a small flask attached to a reflux condenser. About 15 c.c. of water were now added, and the flask was heated for half an hour on the water-bath. The acetylated oil was separated by the addition of a considerable quantity of water to the liquid, which had been transferred to a separating funnel; it was washed with sodium carbonate solution and afterwards with water until the washings were neutral to litmus, and was then dried with anhydrous sodium sulphate. 1.4262 grams of the acetylated oil were hydrolysed with  $N/2$  alcoholic potassium hydroxide, and the resulting solution was titrated with  $N/2$  hydrochloric acid; it was found that 5.9 c.c. of the alkali solution had been neutralised by the acids formed in the hydrolysis, whence the saponification number of the acetylated oil is 115.8, corresponding with 31.85 per cent. of total alcohols (calculated as  $C_{10}H_{17} \cdot OH$ ) in the original oil; 1.1 per cent. of the alcohols being present in the form of esters, the free alcohols amount to 30.75 per cent.

#### *Estimation of Methoxyl.*

The estimation of methoxyl in the oil was effected by a modification of Zeisel's method:

I. 0.3233 gave 0.0281 AgI. OMe = 1.15 per cent.

II. 0.5010 „ 0.0443 AgI. OMe = 1.16 per cent.

#### *Separation of the Terpene.*

The oil (150 grams) was distilled under 10 mm. pressure by means of a paraffin bath, and the distillate was collected until the temperature rose to  $110^\circ$ . The fraction thus obtained was redistilled under the same pressure and collected below  $100^\circ$ . This product was heated with and redistilled from metallic sodium under the ordinary pressure. A specimen of the terpene which had been treated five times in this way gave, on analysis, figures which pointed to the formula  $C_{10}H_{16}$ , but it evidently still contained a small quantity of oxygenated compounds. Unfortunately, the quantity of terpene remaining was too small to admit of further attempts to purify it.

0.2699 gave 0.8586  $\text{CO}_2$  and 0.2731  $\text{H}_2\text{O}$ .  $\text{C} = 86.8$ ;  $\text{H} = 11.3$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

The terpene boils at  $167\text{--}172^\circ$  and has a specific gravity 0.8659 at  $15^\circ/15^\circ$ . Its rotatory power in a 100 mm. tube is  $-15.48^\circ$  or  $[\alpha]_D -17.72^\circ$ . It possesses a pleasant lemon-like and slightly camphoraceous odour, and gives an orange-red coloration with concentrated sulphuric acid.

Determinations of the vapour density by V. Meyer's method, using aniline as the heating agent, gave the following results: I. 0.0612 gram gave 9.3 c.c. at  $17^\circ$  and 755 mm. measured over water. Hence the vapour density = 80.1 and the molecular weight = 160.2. II. 0.1027 gram gave 16.0 c.c. at  $17^\circ$  and 751 mm. measured over water. Hence the vapour density = 78.1 and the molecular weight = 156.2.  $\text{C}_{10}\text{H}_{16} = 136$ . These results are somewhat high, but this is due to polymerisation of some of the terpene with formation of resin in the course of the experiment; the formula  $\text{C}_{10}\text{H}_{16}$  is, however, clearly indicated.

*Preparation of the Dibromide.*—Bromine was added drop by drop to a well cooled solution of the terpene in glacial acetic acid until the colour was no longer discharged. Since nothing had separated from the solution after 24 hours, the product was precipitated by the addition of water and dissolved in ether; the ethereal solution was washed with solution of sodium carbonate and afterwards with water and dried with calcium chloride. After the removal of the ether by distillation, the residue consisted of a nearly colourless, syrupy liquid. It was left over calcium chloride for four weeks in a vacuum desiccator, at the end of which time it had become slightly yellow, but otherwise remained unchanged. Estimation of the bromine by Carius's method showed that the substance is a *dibromide*,  $\text{C}_{10}\text{H}_{16}\text{Br}_2$ .

0.3945 gave 0.5116  $\text{AgBr}$ .  $\text{Br} = 55.2$ .

$\text{C}_{10}\text{H}_{16}\text{Br}_2$  requires  $\text{Br} = 54.1$  per cent.

Attempts to prepare a crystallisable nitrosochloride or nitrosite were unsuccessful.

After the removal of the greater part of the terpene, the residual oil was shaken with solution of sodium carbonate (5 per cent.). Subsequent examination of the solution showed that nothing had been extracted from the oil except a little brown colouring matter; the absence of free acids was thus established.

The oil was washed with water and shaken with a strong solution of sodium hydrogen sulphite for about half an hour; the aqueous liquid was then run off and washed with ether. Since no solid substance separated from the solution, it was treated with an excess of sodium carbonate and distilled. The first few drops of the distillate



had an odour resembling that of fatty aldehydes, and on further distillation a slight citral-like odour was observed, but no appreciable quantity of aldehydes was obtained.

### *Identification of Eugenol.*

The oil was now washed with a small quantity of solution of sodium carbonate and afterwards with water; it was then shaken with about 30 c.c. of solution of sodium hydroxide (5 per cent.). After the aqueous solution had been washed with ether, it was acidified with dilute sulphuric acid. A substance with a clove-like odour separated in oily drops and was extracted with ether. The ethereal solution was dried with calcium chloride and the ether carefully removed by distillation. The residue consisted of about  $1\frac{1}{2}$  grams of a brown oil which gave with ferric chloride the blue colour characteristic of eugenol. It was dissolved in dilute solution of potassium hydroxide, benzoyl chloride was added drop by drop, and the mixture was warmed and well shaken. A benzoyl derivative separated, and was washed with dilute potassium hydroxide, and afterwards with water. When crystallised from alcohol, it formed well-defined, rhombic prisms; it was recrystallised from the same solvent and dried between filter papers. It melted sharply at  $70^{\circ}$ , and, on analysis:

0.1865 gave 0.5179  $\text{CO}_2$  and 0.0997  $\text{H}_2\text{O}$ .  $\text{C} = 75.74$ ;  $\text{H} = 5.94$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 76.12$ ;  $\text{H} = 5.97$  per cent.

Determination of the methoxyl was made by a modification of Zeisel's method:

0.2950 gave 0.2603 AgI.  $\text{OMe} = 11.64$ .

$\text{OMe} \cdot \text{C}_6\text{H}_5(\text{C}_3\text{H}_5) \cdot \text{OBz}$  requires  $\text{OMe} = 11.57$  per cent.

The benzoyl derivative of eugenol was prepared for comparison; this melted at  $70^{\circ}$ , and when mixed with that obtained from the phenol from the oil, the melting point was unchanged.

### *Eugenol Methyl Ether (1).*

After removing the eugenol from the oil by shaking it with aqueous potassium hydroxide, the oil still possessed a pungent taste which closely resembled that of eugenol methyl ether, a small quantity of which was prepared for comparison. Further, since the amount of eugenol present only accounts for a small proportion of the methoxyl found in the oil, some other substance containing methoxy-groups must be present. It is, therefore, highly probable that the oil contains a little eugenol methyl ether; the quantity of this compound demanded

by the percentage of methoxyl (after deducting that due to the eugenol) amounts to about 3 per cent.

*Hydrolysis with Alcoholic Potassium Hydroxide.*

In order to hydrolyse the esters, the oil (from which the terpene and eugenol had been removed) was boiled for two hours with alcoholic potassium hydroxide in a flask connected with a reflux condenser. After the greater part of the alcohol had been removed by distillation, the liquid was transferred to a separating funnel and water was added in sufficient quantity to effect the separation of the oil. The oil which had separated was run off, and the last portions were removed by shaking with ether; the oil was then dissolved in this ether, and the ethereal solution washed with a little water and dried quickly with calcium chloride. After the ether had been removed by distillation, the oil was distilled under 10 mm. pressure and afterwards separated into four fractions (I, II, III, and IV) by distillation under atmospheric pressure.

The alkaline liquid was concentrated to a small volume and was then acidified with sulphuric acid and distilled with steam. The first portion to distil over was turbid and contained small oily drops of a substance with the odour of eugenol; the whole of the distillate was rendered slightly alkaline with sodium carbonate and extracted with successive portions of ether. After distilling off the ether, a small residue of eugenol was obtained, which gave a blue coloration with ferric chloride and yielded a benzoyl derivative melting at 69—70°. A small quantity of eugenol was therefore present in the oil in the form of an ester.

The sodium carbonate solution (from which the eugenol had been extracted) was concentrated, acidified with sulphuric acid, and distilled with steam. The distillate was again neutralised with sodium carbonate, was concentrated to a very small volume, and was acidified with sulphuric acid and shaken repeatedly with ether. The ether was carefully removed by distillation, and a very small residue was obtained, which had a pale brown colour and an odour of fatty acids (especially that of propionic acid); when boiled with a little alcohol and strong sulphuric acid, an ethereal odour recalling that of ethyl propionate was produced.

The four fractions of oil obtained after the hydrolysis of the esters were collected at the following temperatures: I, 200—215°; II, 215—223°; III, 223—232°; IV, 232—255°. After refractionation, six fractions were obtained which boiled within the following ranges of temperature: (1) 195—205°; (2) 205—215°; (3) 215—223°; (4) 223—227°; (5) 227—235°; (6) 235—245°; owing, however, to

the small volume operated on, the separation was necessarily incomplete. The specific gravity and optical rotatory power of each fraction were determined; the results are given in the following table.

| Fraction. | Boiling point. | Specific gravity<br>15°/15°. | $[\alpha]_D$ . |
|-----------|----------------|------------------------------|----------------|
| 1         | 195—205°       | 0·9156                       | - 9·49°        |
| 2         | 205—215        | 0·9468                       | - 6·26         |
| 3         | 215—223        | 0·9756                       | - 3·62         |
| 4         | 223—227        | 1·0019                       | - 2·04         |
| 5         | 227—235        | 1·0027                       | - 1·60         |
| 6         | 235—245        | 1·0272                       | - 1·00         |

#### *Identification of Linalool.*

*Fraction (1).*—The odour of this fraction indicated the presence of some terpene which had not been removed by the earlier treatment; it also possessed a fragrance similar to that of linalool. Five grams of it were added gradually to a solution containing 30 grams of potassium dichromate, 15 grams of sulphuric acid, and 100 c.c. of water, the mixture being kept cool and well shaken. After an hour it was warmed for a short time on the water-bath and then distilled with steam. The distillate contained about 2 grams of an oily liquid, which had an intensely lemon-like odour, due to the presence of citral. The citral was identified by conversion into  $\alpha$ -citryl- $\beta$ -naphthacinchonic acid. The oil from the distillate, after being dried with calcium chloride, was dissolved in dry alcohol; a small quantity of an alcoholic solution of  $\beta$ -naphthylamine and a drop or two of pyruvic acid were added, and the mixture was heated in a flask attached to a reflux condenser for about an hour. On cooling, minute, lemon-yellow plates separated, which were collected and drained on a porous tile. In order to purify this substance, it was dissolved in dilute ammonia and reprecipitated by the addition of acetic acid, was washed with water and recrystallised from hot alcohol; it now melted at 196—198°, and agreed in its general characters with a specimen of the  $\beta$ -naphthacinchonic acid prepared from citral. It is evident, therefore, that this fraction contained linalool. A careful search was made for camphor or borneol in this and the next fraction, but neither could be detected.

#### *Identification of Safrole.*

*Fraction (2).*—When this fraction was oxidised with chromic acid by the method just described, the product was found to contain citral



and piperonal, which were separated by the method described in the following paragraph.

*Fraction (3).*—The products of the oxidation with chromic acid of 8 grams of this fraction were extracted by shaking the mixture with successive portions of ether. The ethereal solution was washed with a little water, then with solution of sodium carbonate, and again with water. The residue obtained after the removal of the ether by distillation had an odour of citral and piperonal; it was treated with solution of sodium hydrogen sulphite, and a bisulphite compound separated in small, glistening plates. This compound was warmed in contact with the solution for about half an hour in order to free the piperonal compound from that of citral, the latter being redissolved under these conditions with formation of sodium citraldihydrosulphonate,  $C_9H_{17}(SO_3Na)_2 \cdot CHO$ , as has been shown by Tiemann and Semmler (*Ber.*, 1893, 26, 2710). The bisulphite compound was now collected and decomposed with solution of sodium carbonate; piperonal separated and was transferred to a filter paper and washed with water. The product possessed the characteristic odour and general properties of piperonal, and after recrystallisation from warm light petroleum melted at  $37^\circ$ . On analysis:

0.2186 gave 0.5116  $CO_2$  and 0.0767  $H_2O$ .  $C = 63.83$ ;  $H = 3.84$ .

$C_8H_6O_3$  requires  $C = 64.00$ ;  $H = 4.00$  per cent.

The formation of piperonal by the oxidation of the oil indicated the presence of safrole, and this was confirmed by the preparation of its nitrosite by the method described by Angeli and Rimini (*Gazzetta*, 1893, 25, ii, 200). About 6 grams of the oil, from fractions (4) and (6), were dissolved in 20 c.c. of light petroleum, and the solution was poured into a flask containing an aqueous solution of sodium nitrite. Dilute sulphuric acid was added slowly, drop by drop, when an opaque, yellowish-brown substance gradually separated at the junction of the liquids. This product was transferred to a filter paper and washed with water, dilute potassium hydroxide, again with water, then with alcohol, and finally with ether. Safrole  $\alpha$ -nitrosite was thus obtained as a pale yellow powder which melted with effervescence at  $129-130^\circ$ , and corresponded in all its characters with a specimen of the nitrosite prepared from safrole. On analysis:

0.1916 gave 0.3538  $CO_2$  and 0.0764  $H_2O$ .  $C = 50.36$ ;  $H = 4.43$ .

$C_{10}H_{10}O_3N_2$  requires  $C = 50.42$ ;  $H = 4.20$  per cent.

In order to test for the presence of terpineol in fraction (3), a portion of it was treated with hydriodic acid of specific gravity 1.95; nothing separated, although an artificial mixture of terpineol with safrole, when treated in the same way, readily furnished the crystalline

dipentene dihydriodide; hence it must be concluded that terpineol is absent.

*Fraction (4).*—This fraction, on oxidation with chromic acid, yielded piperonal, together with a small quantity of citral.

*Fraction (5).*—By the oxidation of this fraction with potassium permanganate according to the method described by Tiemann (*Ber.*, 1891, 24, 2883), a small quantity of piperonylic acid was obtained, which melted at  $226^{\circ}$  (uncorr.), and agreed in its general characters with a specimen of piperonylic acid obtained by oxidising safrole in the same way.

When this fraction was oxidised with chromic acid mixture, piperonal and a little citral were produced. An attempt to detect the presence of geraniol by means of the formation of its diphenylurethane gave a negative result.

### Summary.

This investigation has shown that the chief constituents of the oil are as follows:

- (i) A terpene,  $C_{10}H_{16}$ .
- (ii) Linalool.
- (iii) Safrole.
- (iv) Eugenol.
- (v) Eugenol methyl ether (?).

The quantitative composition (as far as can be judged from the small sample of oil available for examination) is roughly as follows:

|   |                 |
|---|-----------------|
| Terpene .....                                 | 15—20 per cent. |
| Alcohols (wholly, or in part, linalool) ..... | 30    ,,        |
| Esters.....                                   | 1.5    ,,       |
| Safrole .....                                 | 40—50    ,,     |
| Eugenol .....                                 | 1    ,,         |
| Eugenol methyl ether (?) .....                | 3    ,,         |

In conclusion, I desire to express my warmest thanks to Professor Dunstan, both for the suggestion that I should undertake this inquiry and for the encouragement which he has given during the course of the work.

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CVIII.—*Sulphocampholenecarboxylic Acid.*

By ALFRED W. HARVEY and ARTHUR LAPWORTH.

CAMPHOR and its halogen derivatives, when subjected to treatment with sulphuric or chlorosulphonic acid, afford a number of sulphonated compounds, the nature of the product varying greatly according to the exact conditions obtaining during the process.

Cazeneuve (*Bull. Soc. chim.*, 1890, [iii], 4, 715, and 1891, [iii], 5, 651), who appears to have been the first to enter this field, heated  $\alpha$ -chlorocamphor with concentrated sulphuric acid at temperatures between  $30^{\circ}$  and  $70^{\circ}$  and isolated a number of sulphonic derivatives, the majority of which contained only nine of the ten carbon atoms present in the original substance, but these compounds must have arisen as the result of very profound changes in the molecular structure of the camphor molecule. A trisulphonic acid, perhaps of camphor itself, appears to have been obtained by him when working under certain conditions.

Kipping and Pope (*Trans.*, 1893, 63, 548) obtained true sulphonic derivatives of camphor by acting on camphor and its  $\alpha$ -halogen compounds with fuming sulphuric acid or with chlorosulphonic acid (compare also Marsh and Cousins, *Trans.*, 1891, 59, 966). These, as was shown by Kipping (*Trans.*, 1896, 69, 920), contain a sulphonic group attached to the median methyl group of the camphor molecule. A second series of camphorsulphonic acids is obtained by the method of Reyhler (*Bull. Soc. chim.*, 1898, [iii], 19, 120), in which a mixture of acetic anhydride and sulphuric acid is employed as the sulphonating agent; the sulphonic bromide of Reyhler's acid has been found to yield  $\beta$ -bromocamphor when it is decomposed by heat; it is therefore natural to suppose that these substances are  $\beta$ -sulphonic derivatives (Armstrong and Lowry, *Trans.*, 1902, 81, 1445).

When  $\alpha$ -bromocamphor is heated with fuming sulphuric acid, a small quantity of a neutral substance is produced. This substance, which probably has the character of a sultone (Kipping and Revis, *Proc.*, 1896, 12, 247), has not yet been closely investigated.

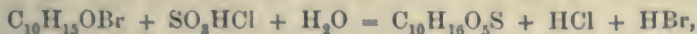
Lastly, there may be mentioned the isomeric camphenesulphonic acids which are produced when camphor is sulphonated with fuming sulphuric acid (Lapworth and Kipping, *Trans.*, 1896, 69, 1546). In the latter cases, nothing is known as to the position occupied by the sulphonic group.

The present communication deals with derivatives of a new product, which is formed in small quantities when  $\alpha$ -bromocamphor is heated



with chlorosulphonic acid in chloroform solution, and occurs as a by-product in the preparation of  $\alpha$ -bromocamphorsulphonic acid by the usual method (Kipping and Pope, *Trans.*, 1895, 67, 356).

The new acid has the formula  $C_{10}H_{16}O_5S$ , and the process by which it arises may be assumed to consist of a change in the bromocamphor of the following character :



and therefore appears to involve both sulphonation and hydrolysis.

It is not possible at present to say with any degree of confidence in what order the sulphonation, removal of hydrogen bromide, and hydrolysis have taken place, but it is difficult to understand how water could have operated effectively before sulphonation is complete and therefore in presence of excess of chlorosulphonic acid ; it seems most probable that a part of the change occurs after the sulphonation product is added to water or heated with the lime used in removing the sulphuric acid.

The compound is a dibasic acid, and occurs in the form of its ammonium hydrogen salt in the mother liquors obtained in the preparation of the ammonium bromocamphorsulphonate. As these liquors have been obtained in the evaporation of a solution originally containing excess of ammonia, it follows that the normal ammonium salt has lost ammonia as the result of hydrolytic dissociation. The acid salt is highly characteristic, but the free acid has not been obtained in a crystalline form, and our experiments have been carried out for the most part with the ammonium salt.

The acid is obviously both a sulphonic acid and a carboxylic acid, and may be represented by the formula  $CO_2H \cdot C_9H_{14} \cdot SO_3H$  ; in consideration of the great difference in the relative strength of the two types of acids, the acid salts must be represented by the formula  $CO_2H \cdot C_9H_{14} \cdot SO_3M$ . The acid chlorides and bromides are highly unstable, being hydrolysed rapidly even by cold water ; they have been obtained only as oils, and no better success has as yet attended any efforts to prepare the amides and esters, and as the supply of material has been very limited we have not thought it worth while to pursue experiments very far in this direction.

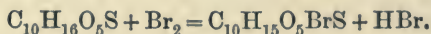
The hydrocarbon,  $C_9H_{16}$ , from which the acid is derived is isomeric with the campholenes, or possibly identical with one of them. In accordance with this view of the structure of the acid, the solutions of its salts instantly decolorise ice-cold potassium permanganate solution and bromine water, so that the compound is undoubtedly of an unsaturated character.

The products of the action of potassium permanganate on the acid have

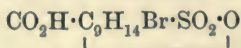
not yielded anything of a crystalline character, and this is scarcely surprising, as the isolation of crystalline derivatives of fatty sulphocarboxylic acids is usually a matter of great difficulty.

It is important, however, to observe that during the oxidation no sulphuric acid is liberated, neither does there appear to be formed any oxalic acid or any acid capable of being extracted with organic solvents from a solution rendered strongly acid by sulphuric acid. It would appear, therefore, that no decomposition into two molecules occurs; hence, in all probability the oxidation results in the opening of an unsaturated ring and the production of an open chain sulphopolycarboxylic acid.

The action of bromine on solutions of the acid or of its salts leads to the formation in almost theoretical amount of a very sparingly soluble bromo-compound,  $C_{10}H_{15}O_5BrS$ , in accordance with the equation:



The new compound crystallises readily from chloroform in well-developed crystals, and exhibits the characteristics of a monobasic acid, a view confirmed by a determination of its equivalent by titration with cold sodium hydroxide. It dissolves in a cold aqueous solution of sodium carbonate, expelling carbon dioxide, and is reprecipitated unchanged on addition of a mineral acid, but if boiled with excess of alkali it slowly loses bromine. The circumstance that it is almost completely precipitated from solution of its salts by mineral acids indicates that it is the carbonyl and not the sulphonic group to which the substance owes its acid properties, so that it may be concluded with certainty that the sulphonic group has become concerned in the formation of a sultone ring. The formula



is therefore to be assigned to the substance.

The bromo-compound yields esters with great ease when warmed with methyl or ethyl alcohol in presence of sulphuric or hydrochloric acid. These esters are well-characterised substances, and the significance which may be attached to their ready formation is referred to elsewhere.

Numerous experiments have been made in the endeavour to obtain the campholenecarboxylic acid itself, or one of its oxidised derivatives, by hydrolysing the sulphonic acid and the products obtained from it after treatment with various oxidising agents. The acid itself does not appear to be hydrolysed to any appreciable extent when superheated steam is passed into a solution in sulphuric acid at 160–180°, or when it is heated in closed tubes with fuming hydrochloric acid at



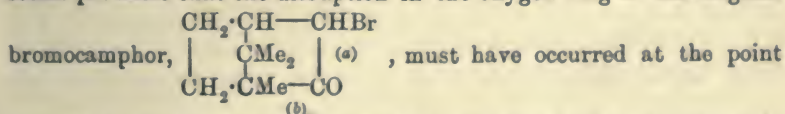
160—200°; in all cases, charring occurred before hydrolysis. With the oxidation products of the sulphonic acid, the carbonisation did not occur to such a marked extent, but again the hydrolysis did not appear to take place at all readily.

On fusing the acid with potassium hydroxide, it was again found that decomposition took place only with great difficulty, the temperature necessary for the production of any large quantity of sulphite being so high that much carbonisation occurred. Better success was met with when the acid was first oxidised with potassium permanganate and the product fused with the alkali. Here very little charring was noticed, and on examining the carboxylic acids produced in the process it was found that one of these yielded a sparingly soluble copper salt, so that its isolation and purification was rendered comparatively easy. Examination of the foregoing acid showed that it was a dibasic acid,  $C_7H_{12}O_4$ , melting at about 85°. It gave a well-defined anhydride which melted at 37—38° and an anilic acid which crystallised in shining, six-sided plates melting at 144°. These properties are characteristic of  $\alpha\alpha$ -dimethylglutaric acid, which is a product obtained during the degradation of  $\beta$ -campholenic acid (Tiemann, *Ber.*, 1895, 28, 2176) and also from sulphocamphylic and isolauronic acids (Perkin, *Trans.*, 1898, 73, 847; and Blanc, *Bull. Soc. chim.*, 1898, [iii], 19, 248).

Whilst it cannot be maintained that the constitution of sulphocampholenecarboxylic acid has been determined with any certainty, there are certain conclusions which we believe may safely be drawn.

In the first place, the formula of the acid indicates that it is probably allied to sulphocamphylic acid,  $C_9H_{15}O_5$ , to which it shows many points of resemblance, and there can be little or no doubt that the substance also contains a closed chain and an ethylenic linking.

Secondly, it is certain that the compound contains the group  $\cdot CH_2 \cdot CO_2H$  or  $\cdot CH \cdot CO_2H$ , probably the former; this conclusion follows from the properties of the bromo-sultone, which is esterified with great readiness when warmed with alcohol and mineral acids. From this, it seems probable that the disruption in the oxygen ring of the original



marked (a), and not at that marked (b), as there can be no reasonable doubt that the origin of the carboxyl group of the acid is the carbonyl group of the parent substance.

Thirdly, the acid does not contain the grouping  $C=CH \cdot CO_2H$ , as it does not afford a trace of oxalic acid when it is oxidised with potassium



permanganate. It seems clear, therefore, that the withdrawal of the bromine atom as hydrogen bromide has given rise to an ethylenic linking at a different position in the molecule, an occurrence which is not at all improbable, for the migration of double linkings is known to occur under conditions far less violent than those under which the acid under consideration is formed. It may be remarked that the removal of the bromine atom has not taken place here in the same manner as during the change by which  $\alpha$ -dibromocamphor affords bromocamphorenic acid, the carboxyl group in that substance being attached to a tertiary carbon atom.

Two series of compounds are already known to be formed by the breaking down of the camphor molecule at the position ( $\alpha$ ), namely, the  $\alpha$ - and the  $\beta$ -campholenic acids and their derivatives. These two classes of compounds are in a manner related to one another, inasmuch as under certain conditions representatives of the  $\beta$ -series may be obtained from those of the  $\alpha$ -series, but the transformation involves a deep-seated change of structure, resulting in the apparent migration of a methyl group.

Now the conversion of an  $\alpha$ -halogen substituted camphor into derivatives of  $\alpha$ - and  $\beta$ -campholenic acid may be accomplished by a series of changes not altogether different in kind from those which appear to occur in the formation of the substance at present under consideration. Thus, by the action of hydrogen bromide,  $\alpha\alpha'$ -dibromocamphor is converted into  $\alpha\beta$ -dibromocamphor and the latter by alkaline hydrolysis made to afford  $\alpha$ -campholenic acid and  $\beta$ -campholenic acid successively. *A priori* therefore, it seems possible, and even probable, that the new substance is derived from one or other of these two acids, and if so it should be possible to ascertain to which series it is related.

A feature which distinguishes the  $\beta$ - from the  $\alpha$ -campholenic series is the optical inactivity of the former. The new acid is optically active, but it must not be forgotten that hydrolysis has been the secondary change, and the introduction of the sulphonic group with an active molecule would almost of necessity have resulted in the production of a new asymmetric carbon atom, and this in the subsequent change may have retained an enantiomorphous character. The real difference in structure between the  $\alpha$ - and  $\beta$ -series is seen clearly in the degradation products of the two series. The former gives rise to a substance which contains the grouping  $\cdot\text{CMe}_2\cdot\text{CH} \begin{smallmatrix} \text{C:} \\ \text{C:} \end{smallmatrix}$ , such as *isocamphoronic* and *terpenylic* acids, and the latter those with  $\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{Ci}$ , as, for instance,  $\gamma$ -acetyldimethylbutyric and  $\alpha\alpha$ -dimethylglutaric acids.





the new compound in a pure condition, partly by mechanical means and also by repeated crystallisation from alcohol.

The substance was thus obtained in large, transparent rhombs or plates, and proved to be a hydrogen ammonium salt of a new acid; the loss of a molecule of ammonia from the normal salt is, of course, to be attributed to hydrolytic dissociation, which would be expected to extend only to the weak salts formed by the carboxylic group.

The investigation of other salts of the acid led to the development of a second method of isolating the compound which in practice was found to be far more expeditious as well as remunerative. The crude mother-liquors in a highly-concentrated state are rendered alkaline with ammonia, heated to boiling in a porcelain basin, and stirred vigorously, while a strong solution of calcium chloride is run in slowly until a sufficiently copious deposit of the calcium salt of the acid has been formed; the whole is filtered while hot through a large Buchner filter. The filtrate is once more heated to boiling and mixed with more calcium chloride solution, the process being repeated until no further deposition occurs, when a further small quantity may sometimes be obtained by the addition of solid calcium chloride.

The calcium salt obtained in these various operations is washed with a very little hot concentrated solution of calcium chloride, and is then sufficiently pure to be converted into ammonium salt by treatment with ammonium carbonate in the usual way.

The solution of the normal ammonium salt is evaporated to dryness to convert it as far as possible into the hydrogen ammonium salt, then dissolved in a little dilute hydrochloric acid, and this solution again evaporated. The residue, which contains a little ammonium chloride, together with the hydrogen ammonium salt, is afterwards worked up by crystallisation from alcohol.

*Ammonium hydrogen sulphocamphenecarboxylate,*



which was thus obtained, did not lose water at  $160^\circ$ , and gave the following results on analysis:

0.2104 gave 0.3503  $\text{CO}_2$  and 0.1335  $\text{H}_2\text{O}$ .  $\text{C} = 45.4$ ;  $\text{H} = 7.0$ .

0.5330 „ 0.0347  $\text{NH}_3$ .  $\text{N} = 5.4$ .

$\text{C}_{10}\text{H}_{19}\text{O}_5\text{SN}$  requires  $\text{C} = 45.3$ ;  $\text{H} = 7.2$ ;  $\text{N} = 5.3$  per cent.

In order to determine its equivalent, it was titrated against  $\text{N}/10$  sodium hydroxide, the number found being 261, whilst that calculated from the above formula is 265.

The compound is very readily soluble in water and somewhat sparingly so in alcohol, and its solutions expel carbon dioxide from carbonates; it crystallises from hot water in brilliant plates, and on spontaneous evaporation of its saturated aqueous solution is deposited in the



form of magnificent transparent prisms or plates which have a lustre like that of calcite.

By cleavage, elongated, six-sided plates are obtained, but the faces and the general form of complete crystals are somewhat ill-defined, and the system to which they belong could not be definitely determined.

For the determination of its rotatory power, 0.4141 gram of the salt was dissolved in 25 c.c. of water; the rotation observed in a 2 dm. tube was  $\alpha_D = -0.23^\circ$ , whence  $[\alpha]_D = -6.9^\circ$ .

The *normal* ammonium salt, prepared by neutralising a solution of the foregoing substance with ammonia and evaporating nearly to dryness, forms slender needles and is excessively soluble in water.

The *potassium* hydrogen salt,  $\text{CO}_2\text{H}\cdot\text{C}_9\text{H}_{14}\cdot\text{SO}_3\text{K}$ , is very readily soluble in water, and crystallises in the form of slender needles; analysis gave:

0.2156 lost only 0.001 gram at  $150^\circ$ , and gave 0.0670  $\text{K}_2\text{SO}_4$ .  $\text{K} = 13.9$ .

$\text{C}_{10}\text{H}_{15}\text{O}_5\text{SK}$  requires  $\text{K} = 13.7$  per cent.

The normal potassium salt was excessively soluble in water and did not crystallise.

The normal *calcium* salt,  $\text{C}_{10}\text{H}_{15}\text{O}_5\text{SCa}$ , is obtained on mixing concentrated solution of the ammonium salt and calcium chloride, adding sufficient ammonia to render the whole faintly alkaline to litmus, and heating to boiling. It is readily soluble in cold water, and somewhat sparingly so in the hot liquid, and is partially precipitated when a concentrated cold solution is heated to boiling. It crystallises in fine needles, which have straight extinction in polarised light:

0.3638 lost only 0.002 at  $150^\circ$ , and gave 0.1697  $\text{CaSO}_4$ .  $\text{Ca} = 13.7$ .

$\text{C}_{10}\text{H}_{15}\text{O}_5\text{SCa}$  requires  $\text{Ca} = 14.0$  per cent.

The normal *barium* salt is readily soluble in water and separates in a crystalline form when its aqueous solution is evaporated on the water-bath; it is apparently not more readily soluble in hot water than in cold. The crystals are small, elongated, four-sided, flat prisms. When these are examined in convergent, polarised light, an axial figure of very wide angle is seen to emerge perpendicularly through the largest faces; if the bisectrix here is the obtuse one, as is most probable, the double refraction is positive. On analysis:

0.5360 lost nothing at  $150^\circ$ , and gave 0.3251  $\text{BaSO}_4$ .  $\text{Ba} = 35.8$ .

$\text{C}_{10}\text{H}_{14}\text{O}_5\text{SBa}$  requires  $\text{Ba} = 35.0$  per cent.

The hydrogen barium and hydrogen calcium salts crystallise in slender needles. The hydrogen magnesium salt was obtained in the form of glistening, elongated plates with weak double refraction and

straight extinction, the relative direction of greatest elasticity and length varying according to the habit of the crystals.

The free acid was prepared by exactly precipitating the metal from a solution of the barium salt by the addition of sulphuric acid and evaporating the filtered solution nearly to dryness. No separation of crystals occurred even after the solutions of various concentrations had remained during several months.

The substance in aqueous solution exhibits the properties of a very strong acid, and dissolves zinc and iron rapidly with evolution of hydrogen. When heated at  $150^{\circ}$ , the acid rapidly became dark brown, but was afterwards completely soluble in alkali, and by no process was it found possible to convert the compound into an isomeric lactone.

*Action of Phosphorus Chlorides and Bromides on Ammonium  
Sulphocampholenecarboxylate.*

When the crystalline ammonium salt of the acid is triturated with phosphorus pentachloride or bromide, rapid action occurs, and if the resulting liquid mass is poured upon ice, it slowly dissolves in the water formed, leaving only a mere trace of oily material, and by extracting the whole with chloroform or ether it is possible to isolate a small quantity of an oily substance, which has the properties of an acid chloride or bromide, but which did not crystallise even after several months, neither did it afford any crystalline amide. Attempts to convert the acid chloride directly into the amide by treating the compound with ammonia, before or after separation from phosphorus oxychloride, were also unsuccessful.

Many efforts were made to eliminate the sulphonic group by hydrolysis with acids in closed tubes, by treatment with phosphorus chlorides at high temperatures, and by fusion with alkalis, but, although small quantities of crystalline compounds were isolated in some cases, the yields obtained have hitherto rendered the investigation of the products impossible.

*Bromodihydrocampholenesultonecarboxylic Acid*,  $\text{CO}_2\text{H} \cdot \text{C}_9\text{H}_{14} \cdot \text{Br} \cdot \text{SO}_2 \cdot \text{O}$

When ammonium hydrogen sulphocampholenecarboxylate dissolved in water is treated with bromine, the latter is at first instantly decolorised until about 1 molecular proportion has been added, after which the action proceeds more slowly. A white, oily precipitate is produced at the same time, and this at first appears to redissolve on shaking, but soon becomes permanent; the addition of bromine should be continued until the amount of insoluble material does not appear to

increase. No trace of sulphuric acid is eliminated during the process. The aqueous liquor is decanted from the oil, which is then dissolved in chloroform, washed once or twice with water, and the solution dried and allowed to evaporate spontaneously, when crystals of the compound are slowly deposited. It may be purified by crystallisation from a mixture of chloroform and light petroleum. On analysis :

0.2398 gave 0.3210  $\text{CO}_2$  and 0.0962  $\text{H}_2\text{O}$ .  $\text{C} = 36.5$  ;  $\text{H} = 4.4$ .

0.2038 „ 0.1185 AgBr.  $\text{Br} = 24.7$ .

$\text{C}_{10}\text{H}_{13}\text{O}_8\text{SBr}$  requires  $\text{C} = 36.7$  ;  $\text{H} = 4.6$  ;  $\text{Br} = 24.5$  per cent.

The substance is very sparingly soluble in light petroleum, somewhat sparingly so in hot benzene ; it is readily dissolved by chloroform, and dissolves freely in ethyl acetate, acetone, or in methyl or ethyl alcohol.

When heated slowly, the compound sinters below  $130^\circ$ , darkens, and finally becomes dark brown in colour, becoming nearly completely fused and decomposed at about  $155^\circ$ . When heated suddenly to  $165^\circ$ , it fuses at once, then darkens and swells considerably, and finally carbonises. For the determination of its optical activity, 0.4078 gram dissolved in 25 c.c. of chloroform was examined in a 2 dm. tube ; a rotation of  $+0.24$  was observed, whence  $[\alpha]_D = +3.70$ .

The presence of a free carbonyl group in the bromo-compound is proved by the observation that the latter dissolved rapidly in cold solution of sodium carbonate, evolving carbon dioxide, and is precipitated unaltered on addition of a mineral acid to a solution of any of its salts. The metallic salts of this acid did not crystallise readily and were not specially investigated ; when boiled with excess of alkalis, the acid loses bromine and yields products whose nature is being investigated. The esters are characteristic and are easily prepared.

The *ethyl ester*,  $\text{CO}_2 \cdot \text{C}_2\text{H}_5 \cdot \text{C}_9\text{H}_{14} \cdot \text{Br} \cdot \text{SO}_2 \cdot \text{O}$ , was prepared by boiling for some hours a solution of the acid in ten times its weight of ethyl alcohol with a few drops of strong sulphuric acid. On cooling and pouring into a large bulk of water, extracting the liquid with purified ether, and washing the latter with dilute alkali, the ester is obtained at once in a crystalline form, and if sufficient ether has not been employed may separate in a solid form during the process of washing, when it is not easily redissolved. It is purified by crystallisation from boiling light petroleum.

The compound dissolves readily in chloroform, acetone, ethyl acetate, alcohol, or benzene, and somewhat sparingly in cold ether or light petroleum. It melts at  $100\text{--}101^\circ$ . Its character is shown by the fact that it is not dissolved by alkalis, even when hot.

It crystallises from light petroleum in small needles and from



chloroform in elongated, brilliant, rectangular plates which occasionally show truncated angles. Their extinction is straight and the double refraction is weak. The direction of greatest elasticity and length appear sometimes parallel and sometimes perpendicular to one another.

When melted on a glass slide below a cover slip, the fused solid does not resolidify if suddenly cooled to the ordinary temperature, but at 90° it slowly sets in large, transparent patches which show aggregate extinction :

0.2520 gave 0.3746 CO<sub>2</sub> and 0.1208 H<sub>2</sub>O. C = 40.5 ; H = 5.3.

C<sub>12</sub>H<sub>19</sub>O<sub>5</sub>BrS requires C = 40.6 ; H = 5.3 per cent.

The *methyl* ester, CO<sub>2</sub>CH<sub>3</sub>·C<sub>9</sub>H<sub>14</sub>Br·SO<sub>2</sub>·O, was prepared in the same manner as the ethyl ester, and was extracted with chloroform as it was found to crystallise from an ethereal extract when the latter is shaken with sodium carbonate. It is best purified by crystallisation from hot ethyl acetate. On analysis :

0.3840 gave 0.5409 CO<sub>2</sub> and 0.1737 H<sub>2</sub>O. C = 38.4 ; H = 5.0.

C<sub>11</sub>H<sub>17</sub>O<sub>5</sub>SBr requires C = 38.7 ; H = 4.9.

The compound is sparingly soluble in ether, and very sparingly so in light petroleum. It does not dissolve when heated with potassium or sodium hydroxide, but is dissolved readily by alcohol, ethyl acetate, chloroform, or benzene. It crystallises from hot ethyl acetate in brilliant, small pyramids, and melts and slowly decomposes at 192—193°. Crushed fragments of the crystals, examined in convergent polarised light, show here and there the interference figure characteristic of a uniaxial crystal or a biaxial crystal of very small axial angle. The double refraction is negative and strong.

#### *Oxidation of Sulphocampholenecarboxylic Acid.*

Potassium permanganate was instantly decolorised at -5° by a dilute solution of the sulphocampholenecarboxylic acid, and the reduction went on until an amount of permanganate had been used which is equivalent to 6 atomic proportions of oxygen, when the colour became persistent and was only removed by warming on the water-bath. If the solution was then freed from manganese dioxide by filtration and concentrated, a viscid mixture of salts remained which failed to yield crystals under any mode of treatment which was adopted, and if the whole was rendered strongly acid by the addition of a mineral acid, it was not found possible to remove any appreciable amount of material by extraction with ether, ethyl acetate, acetone, benzene, or chloroform. Since such a behaviour is incompatible with the presence of simple

carboxylic acids, it must be surmised that the material was almost wholly composed of sulphonic acids, sulpho-carboxylic acids, or their salts.

On acidifying the concentrated alkaline liquor containing the oxidation product with acetic acid, no trace of precipitate was formed on the addition of calcium chloride, hence oxalic acid was not formed; barium chloride afforded only a very slight precipitate, so that sulphuric acid was not present in any important quantity. When steam was passed through the hot oxidation mixture after acidification with sulphuric acid, an acid liquor distilled; this had an acetone-like odour, but a sufficiently large quantity of the acid was not obtained to serve for its identification.

Attempts to prepare crystalline acid bromides, chlorides, esters, or salts from the oxidation product were invariably unsuccessful. On attempting to remove the sulphonic group by hydrolysis of the material with acids at high temperatures, either by using superheated steam or by heating in closed tubes, a small quantity of a sparingly soluble substance was obtained, but its examination did not afford any results of interest.

It was finally decided to investigate the action of fused alkalis on the oxidation product; this process, which with the original substance led to charring, in the present case proceeded rapidly and with very little darkening; both sulphites and sulphates were detected in the fusion product.

In examining the product, the alkaline mass was dissolved in a small quantity of water and treated carefully with a considerable quantity of moderately strong sulphuric acid, the liquid after cooling was separated by filtration from the deposited potassium sulphate, which was thoroughly washed with ether, the latter being then used to extract the liquid in a continuous extraction-apparatus. After some days' treatment, the ether was removed, dried over calcium chloride, and evaporated. An oily residue was left, which, after a time, became semi-crystalline.

As a preliminary investigation of the crystalline material showed that it gave a sparingly soluble copper salt, the whole of the oily mixture of acids was dissolved in water, the solution rendered faintly alkaline with ammonia, and then mixed with a concentrated solution of copper acetate. On boiling, a copious light blue precipitate was obtained, and this was separated by filtration. The filtrate from this salt was freed from copper by means of hydrogen sulphide and evaporated, when only a relatively small quantity of acid material was left, and the examination of this did not lead to any results of interest. The sparingly soluble copper salt was suspended in water and decomposed by means of hydrogen sulphide, and the free acid obtained in the usual way.



On evaporation of its aqueous solution, the acid was deposited in crystals and was purified by recrystallisation from hot fuming hydrochloric acid. It was finally obtained in the form of slender needles, and melted, a little indefinitely, at  $85^{\circ}$ . On analysis :

0.3128 gave 0.6025  $\text{CO}_2$  and 0.3823  $\text{H}_2\text{O}$ .  $\text{C} = 52.5$  ;  $\text{H} = 13.6$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.5$  ;  $\text{H} = 13.3$  per cent.

The equivalent was determined by titration with  $N/10$  sodium hydroxide, using phenolphthalein as indicator ; the number obtained was 80.5, whilst that calculated for an acid of the formula  $\text{C}_7\text{H}_{12}\text{O}_4$  is 80.

The properties of the acid were therefore very similar to those of  $\alpha\alpha$ -dimethylglutaric acid, for although the true melting point of this substance appears to be  $90^{\circ}$ , this has only been observed on one occasion (Perkin and Smith, this vol., 13), and with the synthetical acid (compare also Tiemann, *Ber.*, 1895, 28, 2176 ; Blanc, *Bull. Soc. chim.*, 1898, [iii], 19, 248, and Perkin, *Trans.*, 1898, 73, 847).

For the complete identification of the acid, it was converted into its anhydride by treatment with boiling acetyl chloride ; the product crystallised from a mixture of ethyl chloride and light petroleum in beautiful, glistening, flat needles melting sharply between  $37^{\circ}$  and  $38^{\circ}$ .

From the pure anhydride, the anilic acid was prepared by the usual method ; it crystallised from ethyl formate in well-formed, four- and six-sided leaflets and melted at  $143^{\circ}$ . Perkin (*Trans.*, 1898, 73, 847) gives  $38^{\circ}$  and  $144^{\circ}$  as the melting point of the anhydride and anilic acid of  $\alpha\alpha$ -dimethylglutaric acid.

There can be no doubt, therefore, that the substance obtained from sulphocampholenecarboxylic acid in the manner above described is  $\alpha\alpha$ -dimethylglutaric acid.

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## CIX.—*Optically Active Esters of $\beta$ -Ketonic and $\beta$ -Aldehydic Acids. Part III. Azo-derivatives of Menthyl Acetoacetate.*

By ARTHUR LAPWORTH.

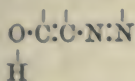
AMONG the numerous types of carbon compounds which exhibit the phenomenon known as tautomerism\* or labile isomerism in virtue of

\* The author employs this term to include all cases of labile isomerism in which a labile hydrogen atom only is concerned, and whether the isomerides are capable of isolation or not. The nomenclature of the subject of isomeric change is at present

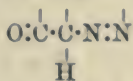


the presence of a labile hydrogen atom, there may be placed that comprising the azo-ketones or α-diketonehydrazones. The question of the tautomerism of these compounds is in a measure involved with that of the *ortho*hydroxyazo-compounds of the aromatic series, and therefore also with that of the related *para*-compounds.

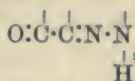
The possible structural configurations of the labile portion of the simple azo-ketones are three in number, namely :



(Azenol)



(Azone)



(Hydrazonone)

of which the first represents the azo-derivative of the *enolic* compound, the second is the true azo-ketone, and the third corresponds with the hydrazone of the α-diketone. The terms suggested for these isomerides do not appear to require special explanation.

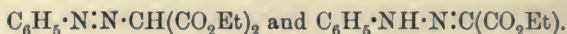
The occurrence of tautomerism in this class of compounds is indicated in the first instance by the fact that in attempting to prepare the possible isomerides one and the same substance is always obtained, the product obtained by the action of phenylhydrazine on an α-diketone being identical with that obtained by treating the corresponding monoketone or its α-carboxylic acid with benzenediazonium salts in alkaline or faintly acid solution. Again, it is well known that the hydrazones prepared from the quinones are identical with the so-called hydroxy-azo-compounds.

Amongst related compounds, the free azo-derivatives of the nitro-paraffins are now regarded as the hydrazones of the nitroaldehydes,  $\text{NO}_2 \cdot \overset{|}{\text{C}} \cdot \overset{|}{\text{N}} \cdot \text{NHPh}$  (Bamberger, *Ber*, 1898, 31, 2626), whilst their sodium derivatives are supposed to be derived from the nitronic acids of the azo-paraffins,  $\text{ONa} \cdot \text{NO} \cdot \overset{|}{\text{C}} \cdot \overset{|}{\text{N}} \cdot \text{NPh}$ .

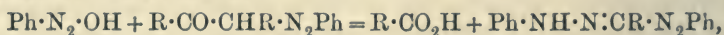
That a labile isomerism subsists between the simple azo-compounds of the paraffins and the isomeric hydrazones has been demonstrated by Fischer (*Ber.*, 1896, 29, 794), who showed that benzeneazoethane,  $\text{C}_6\text{H}_5 \cdot \overset{|}{\text{N}} \cdot \overset{|}{\text{N}} \cdot \text{CH}_2 \cdot \text{CH}_3$ , is converted by sulphuric acid into the hydrazone of acetaldehyde,  $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \overset{|}{\text{N}} \cdot \text{CH} \cdot \text{CH}_3$ .

It is probable that the azo-derivatives of those fatty compounds which contain the grouping  $\cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot$  have been more closely investigated than any other division of the group. In this section, the occurrence of tautomerism is exhibited in a variety of ways, and, as is very general, only one of the free isomerides appears to be produced in each instance. It is well known for example, that the benzeneazo- in a most unsatisfactory state, but as the above word has been mostly used in referring to the cases specified there appears to be no good reason for rejecting it here, although it owes its origin to a mistaken interpretation of the facts.

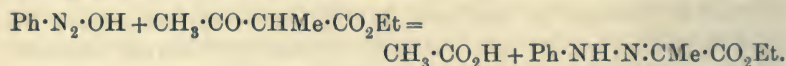
derivative of diethyl malonate is identical with the phenylhydrazone of diethyl mesoxalate, so that it may be presumed that in this case there is a labile isomerism between the forms



In spite of the considerable amount of attention which has been devoted to these compounds, it cannot be claimed that the constitutions of the stable forms have been satisfactorily determined. The greater number of the representatives of this class are capable of reacting with a second molecule of a diazotate, and in the process the molecule breaks down and a formacyl compound is obtained, an *acyl* group being removed :



and a similar process occurs when a diazotate reacts with  $\alpha$ -substituted acetoacetic esters, and a compound which is most probably of a hydrazone type is once more obtained :



Judging, therefore, from the apparently great tendency towards the formation of hydrazones, the most probable view of the constitution of the stable form of the azo-derivatives of acetoacetic esters is that these also are hydrazones. The azo-derivatives of ethyl acetoacetate, however, are dissolved by alkalis, and this observation has recently led to their formulation by Bülow (*Ber.*, 1899, 32, 197) as azones, since their behaviour in this respect resembles that of the parent ester, which, under ordinary circumstances, contains the  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  group almost exclusively. On the other hand, this property really points to the production of the azoenol, as there now seems good reason to believe that the sodium derivatives of the  $\beta$ -diketones and  $\beta$ -ketonic esters are derived from the enolic and not from the ketonic forms. In fact, the behaviour of the azo-compounds with alkalis is quite consistent with the view that the free compounds are hydrazonones, converted by alkalis into azoenols; this assumption has already been made by Betti in a somewhat similar instance (*Ber.*, 1899, 32, 1995), and is exactly similar to the view which Bamberger has taken (*loc. cit.*) of the azo-nitroparaffins.

It is improbable, however, that the question will be finally disposed of until the materials are subjected to a thorough examination by physical methods, but in the present paper the azone formula will be used for the sake of simplicity.

It seemed not unlikely that new light might be thrown on the chemistry of these azo-compounds by an examination of some optically active representatives of high molecular weight, as had already been



done in the case of acetoacetic acid and formylphenylacetic acid (Lapworth and Hann, *Trans.*, 1902, 81, 1491, and 1499), especially since they also might exhibit mutarotation (Lowry, *Trans.*, 1899, 75, 211), a property which would be of some assistance. A number of azo-derivatives of menthyl acetoacetate were therefore prepared for this purpose, but it soon became clear that these would not easily be obtained in more than one isomeric form, since their tendency to assume a crystalline state is so feeble that in all cases the original products persisted as oils during periods of many months; this property is dependent to some extent on their high molecular weight, and it has been observed before (*Trans.*, 1902, 81, 1500) that many menthyl esters crystallise with extreme sluggishness; it is doubtless also in part to be accounted for by the fact that the oils are almost certainly mixtures of several tautomeric and stereochemical forms.

The azo-esters finally obtained are very well-defined compounds with the same light yellow colour which is characteristic of the corresponding ethyl esters. When dissolved in various media, they exhibit mutarotation of an unexpectedly large magnitude. In chemical behaviour, the compounds closely resemble the corresponding ethyl esters, but apparently differ from them in being practically insoluble in aqueous sodium hydroxide, no matter how finely divided they may be. If, however, alkali be added to an alcoholic solution of any of the esters, a deep red coloration is at once produced, and this exactly resembles the tint of aqueous solution of the sodium derivative of the ethyl esters; if, now, water is added to the alcoholic solution, the colour entirely disappears, which is not the case with the ethyl esters. The explanation of this distinction is no doubt that the menthyl ester is much more sparingly soluble in water than are the ethyl esters, so that the amount of free ester in the saturated aqueous solution is smaller than that arising from the hydrolytic dissociation of the sodium compound, hence no chemical difference is indicated by this behaviour.

The initial rotatory powers of the dissolved azo-esters are exceedingly small in comparison with those of the majority of menthyl esters, but rise to values which are of the order usually observed in such cases. [Tschugaeff, who has examined a large number of menthyl esters (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 6069. Compare also *Abstr.*, 1903, ii, 1), has found that their molecular rotations lie within the limits  $[M]_D = 150-290^\circ$  in the case of those derived from monobasic acids, the values being about twice as great in the esters of dibasic acids.]

In the case of the menthyl azoacetoacetates, the initial values for the molecular rotations are about one-third to one-half of the



lower limiting value found by Tschugaeff, and in course of time the values increased to  $2\frac{1}{2}$  to 5 times the original ones.

This observation may be interpreted in more than one way, of which perhaps the most natural is to assume that no general law can yet be held to apply to the rotatory powers of menthyl esters.

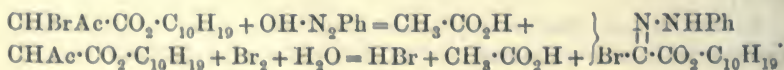
There is a second suggestion, however, which may possibly prove correct, namely, that in the acid residue of these salts there may be an asymmetric carbon atom, which would be the case if the solid compounds had the *azone* formula,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} \begin{smallmatrix} \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19} \\ \text{N} : \text{N} \cdot \text{Ph} \end{smallmatrix}$ . A substance

having this structure, containing as it does the optically active *l*-menthyl radicle, would be capable of existing in two non-superposable forms, which may be designated *dl* and *ll*. Since the asymmetry of the acyl residue arises during the preparation of the azo-compounds, both forms would be produced, and in different amounts. However, the hydrogen attached to the asymmetric carbon atom is labile, so that, owing to the readiness with which tautomeric change occurs, it is only to be expected that when one of these forms begins to separate in the solid state the amount of the second form left in solution would diminish to a corresponding extent in establishing the equilibrium thus disturbed, so that only the first form will be obtained. It will be seen that this is the more likely to occur when it is remembered that it was several months before even one solid form of any of these esters began to be deposited.

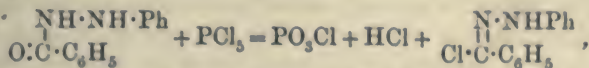
It was hoped that evidence on this point would be obtained if the labile hydrogen atom could be replaced by a non-labile atom or group. The action of bromine on the compounds was therefore investigated, and a series of substances was obtained which, on analysis, gave numbers for carbon and hydrogen in close agreement with those calculated for mono-bromo-derivatives of the original esters.

Later on, however, it was noticed that the analytical numbers agreed equally with those calculated for substances in which an acetyl group had been removed by hydrolysis, and that this had actually taken place was proved by determination of the halogen.

The compounds are also produced when menthyl  $\alpha$ -bromoacetoacetate is treated in alcoholic solution with diazotates, the change here being similar to that which occurs when the  $\alpha$ -alkyl substituted acetoacetic esters are treated in a similar way. Judging by the two modes of preparation, they must be compounds analogous in constitution to the imide chlorides, and their formation may be represented as follows:



They thus belong to a new class of compounds, although one representative of the class of simple hydrazide chlorides has been isolated by Pechmann and Seeberger (*Ber.*, 1894, 27, 322 and 2122), who obtained it by the action of phosphorus pentachloride on β-benzoyl-phenylhydrazine :



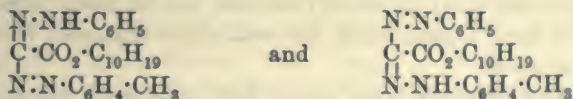
but the substance does not appear to have been very closely investigated.

The new compounds behave chemically, so far as could be ascertained with the small amounts available, in the way which might be anticipated, reacting very readily with cold alkalis, ammonia, and other substances which react easily with acid chlorides and bromides. The closer study of the corresponding ethyl esters will shortly be undertaken, as these will doubtless be far more easily obtained.

It may be added that these compounds, which may be termed "menthyl bromomethylenehydrazonocarboxylates," do not exhibit a trace of mutarotation.

During the course of the work, it was thought desirable to attempt the preparation of some menthyl derivatives of the formazylcarboxylic acids; the ethyl esters of these acids are obtained from the ethyl azoacetoacetates by the action of diazotates in alkaline solution, and it was found that menthyl derivatives were also produced under similar conditions, but apparently with much greater difficulty, and success was met with only in one or two instances.

The formazyl esters may be of a mixed character, that is to say, the second diazo-residue may be different from the first one; thus, if menthyl acetoacetate is treated successively with diazotised aniline and *p*-toluidine, the isomerides



are possible, as well as the bisazo-compound, in which the labile hydrogen is attached to the median carbon atom. The occurrence of isomerism or of mutarotation in such a compound would therefore be of considerable interest, but although mixed formazyl-esters were obtained, no isomerism could be detected, and the solutions were so strongly coloured that no determinations of rotatory power could be made.

## PRACTICAL.

*Menthyl Phenylazoacetoacetate*,  $C_6H_5 \cdot N_2 \cdot CH(CO \cdot CH_3) \cdot CO_2 \cdot C_{10}H_{19}$ .

In preparing this substance, 20 grams of menthyl acetoacetate were dissolved in 500 c.c. of alcohol, and to the ice-cold solution was added 1 molecular proportion of benzenediazonium sulphate dissolved in the smallest possible quantity of ice-water, when the solution, originally colourless, slowly became light yellow in colour. The complete conversion of the ester into its azo-derivative was secured by the gradual addition of excess of finely-powdered sodium acetate to the solution, which was thoroughly shaken and cooled after each such addition. At the end of 24 hours, water was added to dissolve the sodium sulphate, and the precipitated yellow oil repeatedly washed with water.

The product did not deposit a trace of crystalline matter until nearly nine months had elapsed since it had been prepared, but finally set completely to a mass of large, transparent crystals. Portions of this transferred to other preparations of the same substances which had been made by modifications of the above method caused their rapid solidification.

For the purification of the substance, it was crystallised from light petroleum. On analysis :

0.2612 gave 0.6677  $CO_2$  and 0.1881  $H_2O$ . C = 69.7; H = 8.0.

0.2525 „ 0.6497  $CO_2$  „ 0.1840  $H_2O$ . C = 70.1; H = 8.1.

$C_{20}H_{28}O_3N_2$  requires C = 69.8; H = 8.1 per cent.

The compound is readily soluble in cold chloroform, carbon tetrachloride, benzene, ethyl acetate, ethyl formate, or acetone, and somewhat less readily in light petroleum; it dissolves somewhat sparingly in cold ethyl or methyl alcohol, but is much more freely dissolved by these liquids when hot, and often separates from them on cooling as an oil.

The crystals obtained from warm light petroleum are prisms or pyramids with a lemon-yellow colour; from hot alcohol, the substance separates in triangular plates, amongst which remarkable twin forms are frequently noticeable; it is deposited from the cold liquid in the form of prisms, which in polarised light show straight extinction.

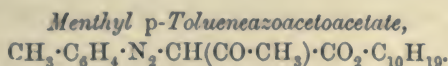
The crushed fragments of the crystals, examined in cedar-wood oil, present the appearance of thin cleavage sheets; if these are observed in convergent polarised light, in most cases, the bisectrix of an interference figure of wide axial angle may be made out. The double refraction is positive and strong.

The compound is not dissolved by cold alkalis either in dilute



or strong solution. If, however, alkali is added to a cold alcoholic solution of the substance, a red coloration appears, similar to that produced under similar conditions by the corresponding ethyl ester; on adding water, however, the substance is reprecipitated, the solution becoming quite colourless; the same behaviour is exhibited by the three closely allied azoacetoacetic esters which are described in this paper.

For the determination of the optical activity of the substance, 0.4046 gram was dissolved in 25 c.c. of benzene; 10 minutes after making up the solution, the rotation in a 2 dm. tube was  $-0.70^\circ$ , whence  $[\alpha]_D = -21.6^\circ$ ; at the end of 8 days, the rotatory power had become constant, the final value being  $[\alpha]_D = -52.5^\circ$ ; the mutarotation was accelerated by traces both of bases and of alkalis.



This substance was prepared by processes exactly similar to those employed in making the corresponding benzeneazo-compound. The oil initially obtained did not crystallise for six months, but finally solidified almost completely. It was purified by crystallisation from light petroleum. On analysis:

0.3238 gave 0.8328  $\text{CO}_2$  and 0.2501  $\text{H}_2\text{O}$ .  $\text{C} = 70.1$ ;  $\text{H} = 8.6$ .

$\text{C}_{21}\text{H}_{30}\text{O}_3\text{N}_2$  requires  $\text{C} = 70.3$ ;  $\text{H} = 8.4$  per cent.

The compound resembles the corresponding benzeneazo-derivative in its general properties, but is rather less soluble in all the ordinary media, and separates in a crystalline form with greater readiness.

It is deposited from alcohol or light petroleum in transparent plates or prisms which melt at  $86-87^\circ$ . The crystals, which separate on rapidly evaporating a drop of the solution on a glass slip, are usually six-sided plates, which are often nearly regular hexagons; and these, when examined in plane-polarised light, extinguish parallel to one pair of sides. Crushed fragments of the larger crystals, in convergent polarised light, frequently show an interference picture, which shows that the crystals are uniaxial or nearly so. The double refraction is strong and positive in sign.

The mutarotation of this compound was studied in a number of different solvents.

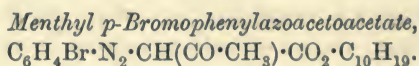
0.4071 gram was dissolved in 25 c.c. of benzene. Eight minutes after solution, its rotatory power was found to be  $[\alpha]_D = -11.8^\circ$ ; after about 3 days, the value had risen to  $36.5^\circ$ , in 5 days to  $59.6^\circ$ , and after 7 days a constant value of  $[\alpha]_D = -61.6^\circ$  was attained.

A similar solution containing 1.6 grams in 100 c.c. of benzene was prepared and divided into three portions, which were placed in tubes.

Observations extending over 24 hours indicated that the mutarotation in each case was taking place at about the same rate. Two of the tubes were opened and one drop of diethylamine and liquid trichloroacetic acid respectively introduced into each, and the subsequent velocities of mutarotation ascertained; in the case of the unopened tube, a gradual fall during a further period of six days was noticeable, the final value being  $[\alpha]_D = -61.3^\circ$ ; with that containing the base, the constant value  $[\alpha]_D = -61.5^\circ$  was attained in less than 20 minutes, and in the third tube the rotation rose to  $[\alpha]_D = -61.3^\circ$  within 4 hours. Acceleration was also found to be produced by primary and tertiary bases and also by bromoacetic acid, salicylic acid, and hydrogen chloride.

The mutarotation in acetone is much more rapid than in benzene; as the substance dissolves somewhat slowly in this medium, it is not possible to obtain the approximate value of the initial specific rotation.

With a solution in acetone containing 0.3999 gram of the compound in 25 c.c., the rotation observed 10 minutes after the first contact of the solid and solvent gave  $[\alpha]_D = -40.64^\circ$ , and at the end of 24 minutes the final value  $[\alpha]_D = -47.9^\circ$  was reached. It was not found very easy to dissolve the compound rapidly and completely in alcohol, ethyl acetate, or ether, but a very distinct mutarotation was observed in each of these media when no attempt was made to employ measured quantities of material, and was always in the sense of an increase in rotatory power.



The oil which resulted on adding sodium acetoacetate to a dilute alcoholic solution of menthyl acetoacetate and p-bromobenzene-diazonium sulphate remained liquid for several months, but crystallised when seeded with the solid p-tolueneazo-ester. It was recrystallised from hot ethyl acetate, and, on analysis:

0.2151 gave 0.4508  $CO_2$  and 0.1223  $H_2O$ .  $C = 57.1$ ;  $H = 6.3$ .

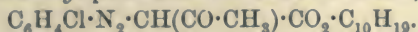
$C_{20}H_{27}O_3N_2Br$  requires  $C = 56.9$ ;  $H = 6.4$  per cent.

The compound is much less sparingly soluble in the ordinary media than are the esters already described; it also shows more distinct tendency to separate in a crystalline form. The crystals obtained by the rapid cooling of the solutions are yellow, transparent, nearly square plates or prisms; if the cooling is very slow, the crystals may attain a considerable size and are often beautifully faceted. They melt at  $119-121^\circ$ .

On examination of crushed fragments of the crystals in convergent polarised light, it is occasionally possible to distinguish interference figures which indicate that the crystal is uniaxial. The double refraction is positive in sign and is strong.

With the purpose of determining the optical behaviour of the substance in solution, 0.7999 gram was dissolved in 50 c.c. of benzene and the resulting solution divided and placed in four tubes; 13 minutes after solution, the rotation observed in one of these was  $[\alpha]_D = -12.84^\circ$ , and did not alter appreciably in 30 minutes; at the end of 24 hours, the rotatory power had risen to  $[\alpha]_D = -17.32^\circ$ . In the two other tubes, the rise was slightly less rapid during the same time, the values  $[\alpha]_D = -16.99^\circ$  and  $-17.14^\circ$  being reached; to the former of these was then introduced a drop of liquid trichloroacetic acid, when a rise to  $-41.34^\circ$  occurred within 25 minutes, and a constant value  $[\alpha]_D = -46.40^\circ$  was attained in about 75 minutes; to the second, a drop of tripropylamine was added, when the rotatory power rose within 1 minute to  $[\alpha]_D = -44.23^\circ$  and became constant at  $-46.68^\circ$  within half an hour. In the case of the unopened tube, about fourteen days elapsed before the rotatory power became constant at  $-46.88^\circ$ .

*Menthyl p-Chlorobenzeneazoacetoacetate,*



This substance became crystalline when seeded with the corresponding *p*-bromo- or *p*-methyl esters, and was purified by crystallisation from ethyl acetate. On analysis:

0.2738 gave 0.6392  $\text{CO}_2$  and 0.1794  $\text{H}_2\text{O}$ .  $\text{C} = 63.7$ ;  $\text{H} = 7.3$ .

$\text{C}_{20}\text{H}_{27}\text{O}_3\text{N}_2\text{Cl}$  requires  $\text{C} = 63.4$ ;  $\text{H} = 7.2$  per cent.

This substance closely resembles the corresponding bromo-compound in appearance, crystalline form, and solubility in different media; it melts, however, at  $103\text{--}105^\circ$ .

Like the preceding esters, this compound exhibits mutarotation. A solution containing 0.4010 gram of the ester in 25 c.c. of benzene had a rotatory power  $[\alpha]_D = -15.43^\circ$ , 8 minutes after the first contact with the solvent, and a gradual increase in rotatory power occurred during 8 days when a constant value  $[\alpha]_D = -55.79^\circ$  had been reached.

*Action of Phenylhydrazine on the Azo-derivatives of Menthyl Acetoacetate. Formation of Azopyrazolones.*

Menthyl benzeneazoacetoacetate dissolved in glacial acetic acid was mixed with excess of phenylhydrazine in the same solvent, and the whole then warmed for about 2 hours on the water-bath; on cooling,



a deposit of brilliant red needles was obtained. These were separated, recrystallised from acetic acid, and, on analysis:

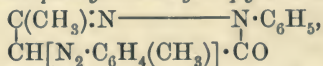
0.2132 gave 0.5391  $\text{CO}_2$  and 0.0994  $\text{H}_2\text{O}$ .  $\text{C} = 69.0$ ;  $\text{H} = 5.2$ .

$\text{C}_{16}\text{H}_{14}\text{ON}_4$  requires  $\text{C} = 69.1$ ;  $\text{H} = 5.0$  per cent.

The substance crystallised in yellow or orange needles or elongated plates. The results of the analysis and the complete absence of optical activity in the solution of the compound having indicated that the menthyl group was absent and that the formation of a pyrazolone ring had taken place, its properties were compared directly with 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone prepared by the ordinary method and were found to be identical in all respects.

The following pyrazolone derivatives were also prepared before their true character was recognised.

*4-p-Methylbenzeneazo-1-phenyl-3-methyl-5-pyrazolone,*



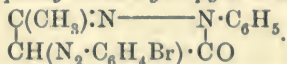
prepared from the *p*-tolueneazo-ester, dissolves sparingly in alcohol and still more sparingly in light petroleum, but is somewhat readily dissolved by glacial acetic acid, acetone, and by hot ethyl acetate. On analysis:

0.2486 gave 0.6403  $\text{CO}_2$  and 0.1218  $\text{H}_2\text{O}$ .  $\text{C} = 70.2$ ;  $\text{H} = 5.5$ .

$\text{C}_{17}\text{H}_{16}\text{ON}_4$  requires  $\text{C} = 69.9$ ;  $\text{H} = 5.5$  per cent.

The substance crystallises from ethyl acetate or acetic acid in flattened needles, which are orange or yellow in colour according as the crystals are small or large. It melts at  $136\text{--}137^\circ$ . When melted on a microscope slide beneath a cover-glass, it solidifies in patches made up of aggregates of plates arranged in fern-like structures. In convergent polarised light, a bisectrix of a biaxial interference figure of large angle may be occasionally made out. The double refraction is moderate.

*4-Bromophenylazo-1-phenyl-3-methyl-5-pyrazolone,*



This substance, which was prepared from the *p*-bromobenzeneazo-ester, somewhat closely resembles the foregoing one in general properties and solubilities. After crystallisation from glacial acetic acid, on analysis:

0.1993 gave 0.3948  $\text{CO}_2$  and 0.0660  $\text{H}_2\text{O}$ .  $\text{C} = 54.03$ ;  $\text{H} = 3.68$ .

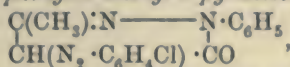
$\text{C}_{16}\text{H}_{13}\text{ON}_4\text{Br}$  requires  $\text{C} = 53.8$ ;  $\text{H} = 3.6$  per cent.

The substance separates from glacial acetic acid in slender, yellow needles which melt sharply at  $152\text{--}153^\circ$ .

The crystals in polarised light extinguish at angles which vary according to their orientation.

Fused in a thin film between glass surfaces, it solidifies slowly in tufts of very fine needles, apparently identical in crystalline form with those obtained by the use of solvents. The double refraction is very strong.

4-Chlorophenylazo-1-phenyl-3-methyl-5-pyrazolone,



prepared from menthyl *p*-chlorobenzeneazoacetate, was purified by crystallisation from hot ethyl acetate. On analysis:

0.3032 gave 0.6819 CO<sub>2</sub> and 0.1224 H<sub>2</sub>O. C = 61.3; H = 4.5.

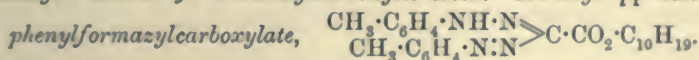
0.1878 „ 0.0852 AgCl. Cl = 11.2.

C<sub>16</sub>H<sub>13</sub>ON<sub>4</sub>Cl requires C = 61.4; H = 4.2; Cl = 11.4 per cent.

The compound is less easily dissolved by most media than the corresponding phenyl and tolyl compounds. It separates from ethyl acetate in well-formed, slender needles, obliquely truncated at their extremities. The crystals, if large, are almost scarlet with a violet surface colour and are strongly dichroic; in polarised light, their extinction directions make an angle of about 45° with their length. It melts at 141–142°.

Melted on a glass slide beneath a cover-slip, the substance solidifies somewhat rapidly to masses of flattened needles; through some of these, one axis of a biaxial interference figure of wide angle emerges nearly normal to the field.

*Action of Diazotates on the Menthylazoacetates. Formation of Menthyl Esters of Formazylcarboxylic Acid. Menthyl pp'-dimethyl-*



In preparing this substance directly from menthyl acetoacetate, an ice-cold alkaline solution of sodium toluenediazotate is added very cautiously to the ester dissolved in alcohol at 10°. The liquid rapidly becomes deep red in colour, and a sparing deposition of a dark, crystalline substance usually takes place; frequently, however, it is necessary to seed the liquid with crystals previously obtained.

The substance may also be prepared in a precisely similar way from the intermediate menthyl *p*-tolueneazoacetate.

It was recrystallised from acetone, and, on analysis:

0.1806 gave 0.4777 CO<sub>2</sub> and 0.1310 H<sub>2</sub>O. C = 72.1; H = 8.1.

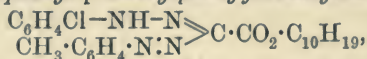
C<sub>25</sub>H<sub>31</sub>N<sub>4</sub>O<sub>2</sub> requires C = 71.9; H = 7.9 per cent.

The compound is readily dissolved by benzene, chloroform, or light petroleum, but less readily by acetone, ethyl acetate, or alcohol. The

crystals, which are well-formed, flattened needles, are dark red in colour and have a blue reflex. In the case of very thin crystals under the microscope, the colour by transmitted light is yellow. It melts at 134—136°.

The colours of the solutions of this substance are very deep red or reddish-yellow according to the concentration; the absorptive power of these solutions for light, even at only 1 per cent. concentration, was found to be too great to admit of the determination of the rotatory power of the material.

*Menthyl p-chlorophenyl-p'-methylphenylformazylcarboxylate,*



was prepared by the action of sodium *p*-chlorodiazotate on menthyl *p*-tolueneazomenthylacetoacetate, and also from sodium *p*-toluenediazotate on menthyl *p*-chlorobenzeneazoacetoacetate. It was crystallised from alcohol and analysed:

0.2392 gave 0.5812 CO<sub>2</sub> and 0.1494 H<sub>2</sub>O. C = 66.3; H = 6.9.

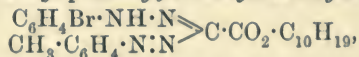
0.1327 „ 0.0419. Cl = 7.8.

C<sub>25</sub>H<sub>31</sub>O<sub>2</sub>N<sub>4</sub>Cl requires C = 66.0; H = 6.8; Cl = 7.8 per cent.

The compound is not very readily soluble in hot or cold alcohol or in cold light petroleum, but it dissolves readily in chloroform and benzene. It separates from hot light petroleum in slender, red or scarlet needles, which, under the microscope, are yellow by transmitted light; it melts at 145—147°.

The crystals in polarised light show straight extinction, and the directions of greatest elasticity and length are at right angles to one another.

*Menthyl p-bromophenyl-p'-methylformazylcarboxylate,*



was made from menthyl *p*-bromobenzeneazoacetoacetate and sodium *p*-toluenediazotate; after crystallisation from alcohol, on analysis:

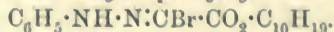
0.2887 gave 0.1089 AgBr. Br = 16.0.

C<sub>25</sub>H<sub>31</sub>O<sub>2</sub>N<sub>4</sub>Br requires Br = 16.2 per cent.

The compound very closely resembles the foregoing one, but crystallises in somewhat larger forms. It melts at 149—151°.

*Action of Bromine on the Azo-derivatives of Menthyl Acetoacetate.*

*Menthyl Bromomethylenephénylhydrazonocarboxylate,*



When bromine was added to this substance dissolved in glacial acetic acid containing excess of sodium acetate, the colour of the



halogen disappeared rapidly until one molecular proportion had been added, when the action seemed to cease. When the whole was poured into water, a colourless oil separated which partially solidified after some weeks. The crystalline material was drained on porous earthenware and crystallised from ethyl formate. On analysis :

0.2792 gave 0.5803  $\text{CO}_2$  and 0.1663  $\text{H}_2\text{O}$ . C = 56.71 ; H = 6.64.

0.3122 „ 0.1528 AgBr. Br = 20.82.

0.2991 „ 0.1466 AgBr. Br = 20.85.

$\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_3\text{Br}$  requires C = 56.7 ; H = 6.6 ; Br = 21.00 per cent.

$\text{C}_{20}\text{H}_{27}\text{O}_3\text{N}_3\text{Br}$  „ C = 56.7 ; H = 6.4 ; Br = 18.9 „ \*

The same substance was prepared by adding benzenediazonium sulphate, dissolved in water, to an ice-cold alcoholic solution of menthyl  $\alpha$ -bromoacetoacetate containing excess of sodium acetate. The oil, which rapidly separated, became semi-crystalline when seeded with a crystal of the compound obtained in the above way.

The ester is somewhat readily soluble in petroleum and in hot alcohol, more readily so in ethyl acetate and formate, and dissolves copiously in chloroform and benzene. It melts at 133—134°.

The compound, when crystallised slowly from ethyl formate, is obtained in large, opaque or opalescent prisms or pyramids; when crushed fragments of these are examined in convergent polarised light, the acute bisectrix of an axial interference figure is occasionally to be seen emerging nearly perpendicular to the field. The appearance of the figure is that characteristic of a crystal with a very powerful axial dispersion, and on closer examination with lights of different wave-lengths, it is found that the dispersion is in reality anomalous, the axial plane for the red, yellow, and green rays being at right angles to those at the violet portion of the visible spectrum; the angle for the red line of lithium is large, for the yellow line of sodium, moderate, and for the green line of thallium, small.

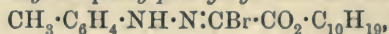
For a determination of the optical activity of the compound, 0.4048 gram was dissolved in benzene and the solution made up to 25 c.c.; the observed deviation in a 2 dm. tube was  $\alpha_D = 2.67^\circ$ , whence  $[\alpha]_D = 82.45^\circ$ .

The compound, like the analogous ones described below, is scarcely affected by a hot aqueous 10 per cent. solution of potassium hydroxide; that this is largely the result of the very sparing solubility of the

\* This and the three following compounds were originally described as simple substitution derivatives of the azoacetoacetic esters (Lapworth, Proc., 1903, 19, 149), the above numbers for carbon and hydrogen having been obtained with the pure materials. The calculated numbers here for the two series are very close, and the halogen determinations which really decide the point were made only after this fact had been realised. The properties of the pure compounds are as previously stated (*loc. cit.*).

compound in water is shown by the fact that if the solution of potassium hydroxide is added to the alcoholic solution of the bromo-ester, an immediate change occurs, even in the cold, indicated by the development of a deep red colour and the formation of potassium bromide in considerable quantity.

*Menthyl bromomethylene-p-tolylphenylhydrazonocarboxylate,*



is made by similar processes in which the corresponding *p*-toluene compounds are used. It was purified by crystallisation from ethyl acetate, and, on analysis :

0.2945 gave 0.6236  $\text{CO}_2$  and 0.1794  $\text{H}_2\text{O}$ .  $\text{C} = 57.8$  ;  $\text{H} = 6.8$ .

0.3028 „ 0.1425 AgBr.  $\text{Br} = 20.0$ .

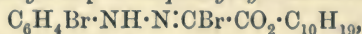
$\text{C}_{19}\text{H}_{27}\text{O}_2\text{N}_2\text{Br}$  requires  $\text{C} = 57.7$  ;  $\text{H} = 6.8$  ;  $\text{Br} = 20.3$  per cent.

$\text{C}_{21}\text{H}_{29}\text{O}_3\text{N}_2\text{Br}$  „  $\text{C} = 57.7$  ;  $\text{H} = 6.6$  ;  $\text{Br} = 18.3$  „

In its general properties and solubility, this substance closely resembles the foregoing one, but it does not exhibit any tendency to separate in opaque forms, and is obtained from ethyl acetate in yellow, transparent pyramids. It melts at  $155\text{--}156^\circ$ . The crystals of this compound also exhibit the phenomenon of anomalous dispersion of the optic axis. The angle is wide for sodium light, and is very small for the red rays, so that with lithium light the interference figure appears nearly that of a uniaxial crystal.

For the determination of its rotatory power, 0.4043 gram was dissolved in 25 c.c. of benzene and the solution examined in a 2 dm. tube. The rotation observed was constant, namely,  $\alpha_D = -2.78^\circ$ , whence  $[\alpha]_D = 86.95^\circ$ .

*Menthyl bromomethylene-p-bromophenylhydrazonocarboxylate,*



was prepared from menthyl  $\alpha$ -bromoacetoacetate and *p*-bromobenzene-diazonium sulphate in presence of sodium acetate. It was purified by crystallisation from ethyl formate, and, on analysis :

0.1633 gave 0.2834  $\text{CO}_2$  and 0.0781  $\text{H}_2\text{O}$ .  $\text{C} = 47.3$  ;  $\text{H} = 5.3$ .

0.2318 „ 0.1900 AgBr.  $\text{Br} = 34.9$ .

0.2380 „ 0.1946 AgBr.  $\text{Br} = 34.8$ .

$\text{C}_{18}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}_2$  requires  $\text{C} = 47.0$  ;  $\text{H} = 5.2$  ;  $\text{Br} = 34.8$  per cent.

$\text{C}_{20}\text{H}_{26}\text{O}_3\text{N}_2\text{Br}_2$  „  $\text{C} = 47.8$  ;  $\text{H} = 5.2$  ;  $\text{Br} = 31.9$  „

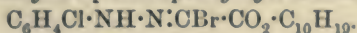
The substance resembles the two foregoing compounds in its solubility and general behaviour. It separates very readily from ethyl formate in brilliantly faceted, transparent prisms or pyramids of considerable size and melts at  $155^\circ$ .

With a solution containing 0.3999 gram of the ester in benzene

(25 c.c.), the rotation in a 2 dm. tube was constant at  $2\cdot35^\circ$ , whence  $[\alpha]_D = -73\cdot45^\circ$ .

The crystals resemble those of the allied compounds in exhibiting anomalous dispersion of the optic axis. With small prisms of the crystals, examined in cedar-wood oil in convergent polarised light, the acute axial bisectrix is found to emerge through one of the longer pinacoid faces. The angle for green light is large, for yellow moderate, and in both cases the plane of the axes is perpendicular to the length of the crystals. The plane for the red rays is at right angles to this, and cuts the crystal along its direction of greatest length; the angle for the red lithium light is small. The double refraction is positive in sign and strong.

*Menthyl Bromomethylene-p-chlorophenylhydrazonocarboxylate,*



This compound was crystallised from ethyl formate, and, on analysis :

0.2883 gave 0.5536  $\text{CO}_2$  and 0.1536  $\text{H}_2\text{C}$ .  $\text{C} = 52\cdot4$  ;  $\text{H} = 5\cdot9$ .

0.2874 „ 0.2270  $\text{AgCl} + \text{AgBr}$ .  $\text{Cl} + \text{Br} = 27\cdot5$ .

$\text{C}_{18}\text{H}_{24}\text{O}_2\text{N}_2\text{ClBr}$  requires  $\text{C} = 52\cdot0$  ;  $\text{H} = 5\cdot8$  ;  $\text{Cl} + \text{Br} = 27\cdot8$  per cent.

$\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2\text{ClBr}$  „  $\text{C} = 52\cdot4$  ;  $\text{H} = 5\cdot7$  ;  $\text{Cl} + \text{Br} = 25\cdot3$  „

This substance is distinguishable only with difficulty from the corresponding *p*-bromo-ester in its general behaviour and solubilities; the crystals are transparent, yellow prisms or pyramids, having apparently the same form as those of the preceding compound. It melts at  $147\text{--}148^\circ$ .

The optic axial dispersion is anomalous. The axial plane for the red lithium line being perpendicular to that for the D line, and the angles for these two rays are not very different in size; the plane for green and blue light is, of course, the same as that for the D line, but the angle is obviously very much larger.

For the rotatory power, 0.4012 gram was dissolved in 25 c.c. of benzene; the rotation observed in a 2 dm. tube was  $\alpha = 2\cdot17$ , hence  $[\alpha]_D = 67\cdot61^\circ$ . The double refraction is strong and positive in sign.

The author desires to express his indebtedness to the Research Fund Committee of the Chemical Society for a Grant which defrayed much of the cost of the preceding investigation.

CHEMICAL DEPARTMENT,

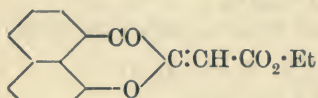
GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.



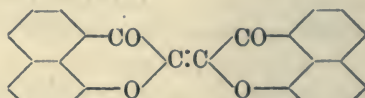
CX.—*Condensation of Phenols with Esters of Unsaturated Acids. Part VIII.*

By SIEGFRIED RUHEMANN.

I RECENTLY showed (Trans., 1902, 81, 419) that the action of ethyl chlorofumarate on the sodium derivative of  $\alpha$ -naphthol yields, together with ethyl  $\alpha$ -naphthoxyfumarate, two compounds, which were then represented by the following formulæ :

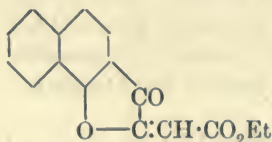


Ethyl naphtharonylacetate.



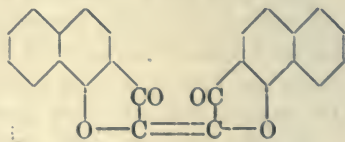
Bisnaphtharonyl.

These symbols seem to agree with the facts that the compounds have properties unlike those of the chromones, and that ethyl chlorofumarate does not form similar substances with  $\beta$ -naphthol. But considerations, based on experiments which are described in the present communication, have induced me to change this view, and to assign to these compounds the following constitutions :



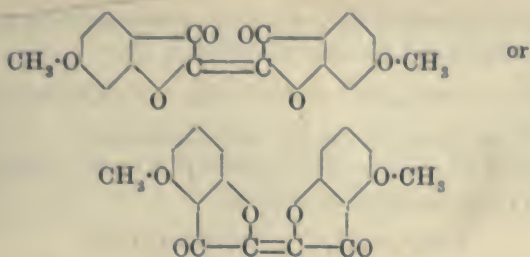
Ethyl naphtharonylacetate.

and

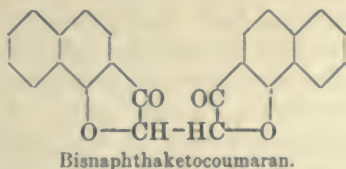


Bisnaphtharonyl.

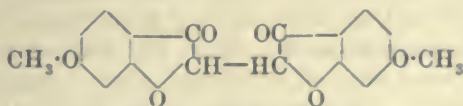
They are therefore to be regarded as derivatives of  $\alpha$ -naphthaketo-coumaran,  $C_{10}H_6 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CH_2$ . This view is supported by the results obtained in the course of further research on the action between ethyl chlorofumarate and the sodium derivatives of the phenols. Guaiacol, as shown before (*loc. cit.*), reacts with the ester to form only ethyl guaiacoloxymumarate, but I find that its isomeride, the monomethyl ether of resorcinol, furnishes, besides ethyl *m*-methoxyphenoxyfumarate, an orange-coloured substance, which has the composition  $C_{18}H_{12}O_6$ . Its constitution can only be represented by one of the following symbols :



The compound, therefore, is a derivative of ketocoumaran (coumaranone),  $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown O \diagup \end{smallmatrix} CH_2$ ; it may be called *dimethoxybisbenzaronyl*. It has properties so much like those of bisnaphtharonyl as to justify the view that both compounds are similarly constituted, and that bisnaphtharonyl is to be regarded as a derivative of  $\alpha$ -naphthaketocoumaran. Dimethoxybisbenzaronyl is very sparingly soluble in alcohol or glacial acetic acid, but readily dissolves in boiling nitrobenzene, its solution having a green fluorescence; it is insoluble in cold aqueous caustic potash, but on prolonged boiling it passes into solution, and is precipitated unchanged on adding a mineral acid. These properties closely resemble those which I have recorded for bisnaphtharonyl (Trans., 1902, 81, 423). Furthermore, both compounds exhibit the same behaviour towards zinc dust and acetic acid, adding on 1 molecule of hydrogen to yield almost colourless substances, which are to be represented thus:



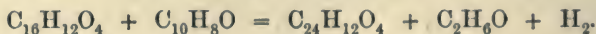
Bisnaphthaketocoumaran.



Dimethoxybisketocoumaran.

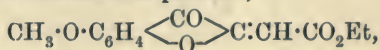
These reduction products readily become oxidised and turn red, as does  $\alpha$ -naphthaketocoumaran (Ullmann, *Ber.*, 1897, 30, 1468). With regard to the formation of bisnaphtharonyl, the view has been expressed (*loc. cit.*) that it takes place by the condensation of 2 mols. of ethyl naphtharonylacetate and the loss of ethyl fumarate. The latter ester, however, is not produced; moreover, it seems to be most probable that bisnaphtharonyl is the result of the union between

ethyl naphtharonylacetate and  $\alpha$ -naphthol, accompanied by the removal of 1 mol. of alcohol and 2 atoms of hydrogen, thus :



The fate of the hydrogen has not been ascertained.

The formation of dimethoxybisbenzaronyl is to be explained in the same manner ; the intermediate product,



however, has not yet been isolated.

Although the monomethyl ether of resorcinol differs from guaiacol in its behaviour towards ethyl chlorofumarate, yet with ethyl phenylpropionate it reacts like the other phenols, and yields ethyl *m*-methoxy- $\beta$ -phenoxy-cinnamate,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}(\text{C}_6\text{H}_5):\text{CH}\cdot\text{CO}_2\text{Et}$  ; the corresponding acid loses carbon dioxide and forms *m*-methoxyphenoxy-styrene.

The diethyl ether of phloroglucinol, also, has been subjected to the action of ethyl chlorofumarate, as well as to that of ethyl phenylpropionate, and in this way ethyl diethoxyphenoxyfumarate and the corresponding derivative of cinnamic acid have been produced.

#### EXPERIMENTAL.

##### *Action of the Monomethyl Ether of Resorcinol on Ethyl Chlorofumarate.*

Sodium (1 atom) dissolves fairly readily in an excess (about 2 mols.) of the hot ether, and, on gradually adding ethyl chlorofumarate (1 mol.) to the solution, a reaction takes place, which is indicated by the development of heat. The product is allowed to cool, and then agitated with ether and dilute sulphuric acid, when an orange-coloured solid separates, which is dimethoxybisbenzaronyl. The ethereal extract, which has a red colour and an intensely deep green fluorescence, contains *ethyl m-methoxyphenoxyfumarate*. From the ethereal solution, after removing the ether, a dark oil is obtained, which is fractionated under diminished pressure. The first portion of the distillate is a colourless liquid, then a viscous, yellow oil passes over, leaving an almost black residue. The yellow oil, when redistilled, boils at 206–207° under 12 mm. pressure :

0.2075 gave 0.4680  $\text{CO}_2$  and 0.1175  $\text{H}_2\text{O}$ .  $\text{C} = 61.51$  ;  $\text{H} = 6.29$ .

$\text{C}_{15}\text{H}_{18}\text{O}_6$  requires  $\text{C} = 61.22$  ;  $\text{H} = 6.12$  per cent.

*Dimethoxybisbenzaronyl*.—The orange-coloured solid, referred to before, dissolves in boiling nitrobenzene, and, on cooling, crystallises in needles which melt at 310° to a dark liquid :



0.2075 gave 0.5073  $\text{CO}_2$  and 0.0695  $\text{H}_2\text{O}$ .  $\text{C} = 66.67$ ;  $\text{H} = 3.72$ .

$\text{C}_{18}\text{H}_{12}\text{O}_6$  requires  $\text{C} = 66.67$ ;  $\text{H} = 3.70$  per cent.

As already indicated, this substance is insoluble in cold aqueous caustic potash, but gradually dissolves on boiling to a yellowish-brown solution. This liquid, when mixed with an excess of hydrochloric acid, furnishes an orange-coloured precipitate, which, by its properties and the following analysis, is characterised as unaltered dimethoxybisbenzaronyl:

0.1476 gave 0.3610  $\text{CO}_2$  and 0.0520  $\text{H}_2\text{O}$ .  $\text{C} = 66.70$ ;  $\text{H} = 3.91$ .

$\text{C}_{18}\text{H}_{12}\text{O}_6$  requires  $\text{C} = 66.67$ ;  $\text{H} = 3.70$  per cent.

*Reduction of Dimethoxybisbenzaronyl and Bisanaphtharonyl.*

*Dimethoxybisketocoumaran.*—On boiling dimethoxybisbenzaronyl with zinc dust and glacial acetic acid for some time, the solution loses its green fluorescence and becomes yellow. The filtrate from the excess of zinc dust, when mixed with water, yields a faintly-coloured precipitate, which readily dissolves in glacial acetic acid, boiling acetone, or alcohol. From the latter solvent, the substance crystallises in colourless plates, which melt at  $166^\circ$  and rapidly turn red:

0.2102 gave 0.5104  $\text{CO}_2$  and 0.0822  $\text{H}_2\text{O}$ .  $\text{C} = 66.22$ ;  $\text{H} = 4.34$ .

$\text{C}_{18}\text{H}_{14}\text{O}_6$  requires  $\text{C} = 66.25$ ;  $\text{H} = 4.29$  per cent.

The molecular weight has been kindly determined by Mr. George Barger by his microscopic method (Proc., 1903, 19, 121).

Acetone was used as the solvent and benzil as the standard: a solution of 0.0315 gram of the substance in 1.312 c.c. of acetone is isotonic with a solution in acetone of  $0.0775 \times 210$  grams of benzil per litre; therefore  $M = 309$ , as compared with 326 required for  $\text{C}_{18}\text{H}_{14}\text{O}_6$ .

*Bisanaphthaketocoumaran.*—Bisanaphtharonyl, when boiled with zinc dust and acetic acid, gradually dissolves yielding a yellow solution. This gives with water a precipitate which crystallises from alcohol in grey needles melting with decomposition at  $218^\circ$ :

0.1435 gave 0.4135  $\text{CO}_2$  and 0.0505  $\text{H}_2\text{O}$ .  $\text{C} = 78.58$ ;  $\text{H} = 3.91$ .

$\text{C}_{24}\text{H}_{14}\text{O}_4$  requires  $\text{C} = 78.68$ ;  $\text{H} = 3.81$  per cent.

This substance, like the foregoing reduction product, is readily oxidised in solution developing a reddish-violet coloration.

*Action of Ethyl Phenylpropiolate on the Monomethyl Ether of Resorcinol*  
*Ethyl m-Methoxy-β-phenoxy-cinnamate.*

This compound is formed by dissolving sodium (1 atom) in an excess of the methyl ether of resorcinol (about 2 mols.) and adding ethyl phenylpropiolate (1 mol.) to the hot solution. The dark product, which is thus produced, is agitated with dilute sulphuric acid and extracted with ether; the ethereal solution is shaken successively with an excess of caustic alkali and water, dried over calcium chloride, and the ether evaporated. The viscous, dark brown residual oil, which is fractionated under diminished pressure (12 mm.), passes over almost entirely between 220° and 235°, and on redistillation a yellow oil is obtained which boils at 232—234° under 12 mm. pressure:

0.2042 gave 0.5426 CO<sub>2</sub> and 0.1123 H<sub>2</sub>O. C = 72.42; H = 6.11.

C<sub>18</sub>H<sub>18</sub>O<sub>4</sub> requires C = 72.48; H = 6.04 per cent.

*m-Methoxy-β-phenoxy-cinnamic Acid*, CH<sub>3</sub>·O·C<sub>6</sub>H<sub>4</sub>·O·C(C<sub>6</sub>H<sub>5</sub>):CH·CO<sub>2</sub>H.

The hydrolysis of the ester is readily effected by digesting it with alcoholic potash for 1 to 2 hours. After distilling off the alcohol on the water-bath, the successive addition of water and an excess of dilute hydrochloric acid to the residue causes the precipitation of the organic acid as a yellow oil which gradually solidifies. The hot solution of this acid in dilute alcohol, after treatment with animal charcoal, yields, on cooling, an emulsion which is slowly transformed into a mass of colourless needles. These dissolve with great ease in organic solvents; they soften at 104° and melt at 110° with evolution of carbon dioxide:

0.2010 gave 0.5248 CO<sub>2</sub> and 0.0940 H<sub>2</sub>O. C = 71.20; H = 5.19.

C<sub>18</sub>H<sub>14</sub>O<sub>4</sub> requires C = 71.11; H = 5.18 per cent.

*m-Methoxyphenoxy-styrene*, CH<sub>3</sub>·O·C<sub>6</sub>H<sub>4</sub>·O·C(C<sub>6</sub>H<sub>5</sub>):CH<sub>2</sub>, is formed on heating the acid under diminished pressure, when it distils at 199—200° under 16 mm. pressure as a colourless oil which possesses an aromatic odour:

0.2030 gave 0.5933 CO<sub>2</sub> and 0.1150 H<sub>2</sub>O. C = 79.70; H = 6.29.

C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> requires C = 79.65; H = 6.19 per cent.

*Ethyl 1 : 3-Diethoxyphen-5-oxyfumarate*,  
 C<sub>6</sub>H<sub>3</sub>(O·C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>·O·C(CO<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>):CH·CO<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>.

The diethyl ether of phloroglucinol, which is required for the preparation of this substance, has been obtained according to the directions of Weidel and Pollak (*Monatsh.*, 1897, 18, 346). Its

sodium derivative is formed by adding the ether (1 mol.) to a solution of sodium (1 atom) in absolute alcohol and removing the alcohol by distillation under diminished pressure. The solid which remains is boiled with a mixture of ethyl chlorofumarate (1 mol.) and toluene for an hour, the product allowed to cool, and, after treatment with dilute sulphuric acid, extracted with ether; the ethereal solution is washed with alkali, then with water, and dried over calcium chloride. The oil, which is left behind after evaporating off the ether, is fractionated under diminished pressure; the larger portion distils at 238—240° under 15 mm. pressure as a yellow, viscous oil:

0·2120 gave 0·4777 CO<sub>2</sub> and 0·1298 H<sub>2</sub>O. C = 61·45; H = 6·80.  
 C<sub>13</sub>H<sub>24</sub>O<sub>7</sub> requires C = 61·36; H = 6·81 per cent.

*Ethyl 1:3-Diethoxyphen-5-oxycinnamate,*  
 C<sub>6</sub>H<sub>3</sub>(O·C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>·O·C(C<sub>6</sub>H<sub>5</sub>):CH·CO<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>.

This compound, which is formed from the diethyl ether of phloroglucinol and ethyl phenylpropiolate in a manner similar to the former ester, is a yellow, viscous oil boiling at 263—264° under 17 mm. pressure:

0·2010 gave 0·5228 CO<sub>2</sub> and 0·1240 H<sub>2</sub>O. C = 70·93; H = 6·85.  
 C<sub>21</sub>H<sub>24</sub>O<sub>5</sub> requires C = 70·79; H = 6·74 per cent.

In conclusion, I may state that, after having recognised bisnaphtharonyl and dimethoxybisbenzaronyl as derivatives of ketocoumaran and α-naphthaketocoumaran respectively, and as compounds which, in the oxygen series, correspond with the members of the indigo group, I have undertaken the study of ketocoumaran and its homologues in the hope of arriving at a general method of preparation of bisbenzaronyl and its derivatives.

GONVILLE AND CAIUS COLLEGE,  
 CAMBRIDGE.

## CXI.—*Action of Phosphorus Trichloride on the Aromatic Ethers of Glycerol. Part II.*

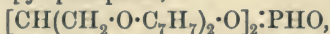
By D. R. BOYD.

IN a previous communication (Trans., 1901, 79, 1221), it has been shown by the author that *s*-glycerol diaryl ethers, when treated successively with excess of phosphorus trichloride and water, are



converted to a large extent into diaryloxyisopropylphosphorous acids,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{Ar})_2 \cdot \text{OPH}_2\text{O}_2$ .

The reaction has now been studied in cases where the phosphorus trichloride and the glycerol ether react in the proportion of one molecule of trichloride to two and three molecules respectively of the ether. The course of the reaction can be followed most conveniently in the case of *s*-glycerol di-*o*-tolyl ether, because the principal product, bisdi-*o*-tolylloxyisopropyl phosphite,



is crystalline and readily separated in an almost pure condition.

It was found that when two molecules of the di-*o*-tolyl ether reacted with one molecule of phosphorus trichloride, the yield of bisdi-*o*-tolylloxyisopropyl phosphite obtained on treatment with water corresponded with about 56 per cent. of the phosphorus trichloride, whilst 12 per cent. of the trichloride was converted into di-*o*-tolylloxyisopropylphosphorous acid.

When three molecules of *s*-glycerol di-*o*-tolyl ether were used, the yield of crystallised bisdi-*o*-tolylloxyisopropyl phosphite corresponded with about 75 per cent. of the phosphorus trichloride, and no appreciable quantity of di-*p*-tolylloxyisopropylphosphorous acid was formed. The principal reaction in the latter case may therefore be represented by the equation :



This result is in harmony with the observations of Milobendski (*Chem. Centr.*, 1899, i, 249) on the behaviour of isopropyl alcohol towards phosphorus trichloride.

From *s*-glycerol di-*p*-tolyl ether, a crystalline bisdi-*p*-tolylloxyisopropyl phosphite was also obtained, but the product in the case of the diphenyl ether was an oil which could not be distilled without decomposition.

The bisdiaryloxyisopropyl phosphites, which have been isolated, are comparatively stable substances; they have no acid reaction and are insoluble in ammonia. On boiling with caustic soda solution, they are hydrolysed, giving rise to phosphorous acid and the original ether.

Incidentally, the diaryloxyisopropylphosphorous acids, which are found to be monobasic, have been more fully characterised by the preparation of certain of their salts.

*Salts of Diphenoxyisopropylphosphorous Acid,*  
 $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{O} \cdot \text{PHO}(\text{OH}).$

The *calcium* salt, which was obtained as a bulky, amorphous precipitate on adding calcium chloride to an alkaline solution of the acid in ammonia, slowly became crystalline; after washing, it was dried in the air and analysed:

0.4938 lost at  $100^\circ$  0.0148  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 2.99$ .

0.5000 gave 0.0404  $\text{CaO}$ .  $\text{Ca} = 5.70$ .

$(\text{C}_{15}\text{H}_{16}\text{O}_5\text{P})_2\text{Ca}, \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 2.67$ ;  $\text{Ca} = 5.95$  per cent.

The salt, when crystallised from a mixture of alcohol and water, separates in needles containing two molecules of water of crystallisation.

The *aniline* salt,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_5$ , is obtained either by adding a solution of aniline hydrochloride to a solution of the acid in ammonia, from which the excess of ammonia has been boiled off, or by mixing molecular proportions of aniline and acid dissolved in alcohol. It crystallises from chloroform to which some light petroleum has been added in needles melting at  $113-114^\circ$ :

0.1264 gave 4.0 c.c. of moist nitrogen at  $20^\circ$  and 754 mm.  $\text{N} = 3.59$ .

$\text{C}_{21}\text{H}_{24}\text{O}_5\text{NP}$  requires  $\text{N} = 3.50$  per cent.

The *p-toluidine* salt,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_3 \cdot \text{C}_7\text{H}_7$ , was prepared in a similar way; it crystallised from its alcoholic solution on the addition of water in needles melting at  $119-120^\circ$ :

0.3802 gave 11.0 c.c. of moist nitrogen at  $19.5^\circ$  and 742 mm.  $\text{N} = 3.24$ .

$\text{C}_{22}\text{H}_{26}\text{O}_5\text{NP}$  requires  $\text{N} = 3.38$  per cent.

*s-Glycerol Di-o-tolyl Ether ( $\beta$ -Hydroxy- $\alpha\gamma$ -di-o-tolyloxypropene),*  
 $\text{C}_7\text{H}_7 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7.$

Epichlorohydrin (27 grams) was added to alcohol in which rather more than the theoretical quantities of *o*-cresol and sodium had been dissolved; the mixture was boiled in a reflux apparatus for about 24 hours, and then poured into water. The oil which separated was extracted with ether, the ethereal solution dried over potassium carbonate, and the oily residue left after evaporating off the solvent was distilled under diminished pressure. After two distillations, the *s*-glycerol di-*o*-tolyl ether was obtained as an almost colourless oil, which boiled at  $226^\circ$  under 13 mm. pressure and slowly changed to a mass of

prismatic crystals melting at 36—37°. The yield was 30 grams, or about 37 per cent. of the calculated amount:

0.1825 gave 0.5018 CO<sub>2</sub> and 0.1230 H<sub>2</sub>O. C = 74.99; H = 7.56.

C<sub>17</sub>H<sub>20</sub>O<sub>3</sub> requires C = 74.94; H = 7.42 per cent.

*Di-o-tolyloxyisopropylphosphorous Acid*, CH(CH<sub>2</sub>·O·C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>·O·PH<sub>2</sub>O<sub>2</sub>.

This substance is the principal product obtained when *s*-glycerol di-*o*-tolyl ether is treated with excess of phosphorus trichloride, and the resulting oil decomposed with water.

A mixture of 16 grams of *s*-glycerol di-*o*-tolyl ether (1 mol.) and an approximately equal quantity of phosphorus trichloride (2 mols.) was heated in a water-bath until reaction ceased, and then poured into water; the white, viscous mass thus obtained, when washed, was warmed with ammonia solution until the bulk dissolved, leaving a crystalline, insoluble substance which weighed 3.7 grams, and was afterwards found to consist chiefly of bisdi-*o*-tolyloxyisopropyl phosphite. The filtrate, on acidification with hydrochloric acid, gave an oily precipitate of di-*o*-tolyloxyisopropylphosphorous acid, the yield being about 11 grams. When obtained in this way, the acid solidifies somewhat slowly, but a solution of the oily precipitate in ethyl acetate, when allowed to evaporate, yields the compound in a crystalline form.

On recrystallisation from the same solvent, the acid was obtained in prisms melting at 88—89°:

0.4714 gave 0.1555 Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. P = 9.18.

C<sub>17</sub>H<sub>21</sub>O<sub>5</sub>P requires P = 9.23 per cent.

Di-*o*-tolyloxyisopropylphosphorous acid readily dissolves in alcohol and in hot ethyl acetate, and in its general properties is very similar to the acids of this type already described.

The *calcium* salt crystallises from dilute alcohol in needles:

0.7139 lost at 100° 0.0641 H<sub>2</sub>O. H<sub>2</sub>O = 8.98.

0.7412 gave 0.0550 CaO. Ca = 5.30.

(C<sub>17</sub>H<sub>20</sub>O<sub>5</sub>P)<sub>2</sub>Ca·4H<sub>2</sub>O requires H<sub>2</sub>O = 9.20; Ca = 5.12 per cent.

The *aniline* salt, CH(CH<sub>2</sub>·O·C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>·O·PHO·ONH<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>, crystallises from carbon disulphide, on adding light petroleum, in prismatic needles melting at 99—100°:

0.2987 gave 7.95 c.c. of moist nitrogen at 16.5° and 747 mm. N = 3.04.

C<sub>23</sub>H<sub>28</sub>O<sub>6</sub>NP requires N = 3.27 per cent.

The *p*-toluidine salt, CH(CH<sub>2</sub>·O·C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>·O·PHO·ONH<sub>3</sub>·C<sub>7</sub>H<sub>7</sub>, crys-



tallises from the same mixture of solvents in clumps of prisms melting at 49—50°:

0.2781 gave 8.1 c.c. of moist nitrogen at 18° and 749 mm.  $N = 3.31$ .

$C_{24}H_{30}O_5NP$  requires  $N = 3.17$  per cent.

*Bisdi-o-tolyloxyisopropyl Phosphite*,  $[CH(CH_3 \cdot O \cdot C_7H_7)_2 \cdot O]_2 \cdot PHO$ .

As already indicated, this substance is produced to some extent by the action of water on the product resulting from the interaction of *s*-glycerol di-*o*-tolyl ether with excess of phosphorus trichloride; it is obtained in larger quantity when two or three molecular proportions of the ether react with one of phosphorus trichloride.

A mixture of 10.2 grams of *s*-glycerol di-*o*-tolyl ether (2 mols.) and 2.5 grams of phosphorus trichloride (1 mol.), when heated on the water-bath until hydrogen chloride was no longer evolved, formed a colourless and very viscous oil, which, on warming with dilute ammonia, soon changed to a mass of crystals. This product was collected, washed with water, dried, and dissolved in boiling ethyl acetate, from which, on cooling, it separated quickly in prismatic needles melting at 118—119°; the yield was 6.2 grams:

0.1758 gave 0.4434  $CO_2$  and 0.1076  $H_2O$ .  $C = 68.79$ ;  $H = 6.86$ .

0.4853 „ 0.0918  $Mg_2P_2O_7$ .  $P = 5.27$ .

$C_{34}H_{30}O_7P$  requires  $C = 69.11$ ;  $H = 6.67$ ;  $P = 5.25$  per cent.

Bisdi-*o*-tolyloxyisopropyl phosphite, which is moderately soluble in benzene and in boiling alcohol, dissolves more easily in hot ethyl acetate, and is practically insoluble in ether; its alcoholic solution shows no acid reaction.

*s*-Glycerol Di-*m*-tolyl Ether ( $\beta$ -Hydroxy- $\alpha\gamma$ -di-*m*-tolyl oxypropane),

$C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot C_7H_7$ .

Epichlorohydrin (60 grams) was boiled for several days in a reflux apparatus with equivalent quantities of *m*-cresol and sodium ethoxide dissolved in alcohol, the product being treated as in the case of the ortho-compound. After three distillations, an almost colourless oil was obtained which boiled at 232° under 13 mm. pressure and did not crystallise; the yield was 41 grams:

0.1911 gave 0.5233  $CO_2$  and 0.1291  $H_2O$ .  $C = 74.68$ ;  $H = 7.57$ .

$C_{17}H_{20}O_3$  requires  $C = 74.94$ ;  $H = 7.42$  per cent.

*Di-m-tolyloxyisopropylphosphorous Acid*,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PH}_2\text{O}_2$ .

Twelve grams of *s*-glycerol di-*m*-tolyl ether were treated with excess of phosphorus trichloride, and the product, on pouring the mixture into water, was digested with warm ammonia solution until the oil present separated, so that the clear ammoniacal liquid could be decanted. On adding hydrochloric acid to this solution, the di-*m*-tolyloxyisopropylphosphorous acid separated as an oil which slowly solidified; the yield was about 6 grams. This acid exhibits less tendency to crystallise than its ortho- and para-isomerides; it is very easily soluble in ethyl acetate, and, as the solvent evaporates, is deposited as a mass of filaments. From a solution in carbon disulphide, however, to which some light petroleum has been added, it separates slowly in clusters of needles melting at 85—87°:

0.5440 gave 0.1821  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{P} = 9.32$ .

$\text{C}_{17}\text{H}_{21}\text{O}_5\text{P}$  requires  $\text{P} = 9.23$  per cent.

The *aniline* salt,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_5$ , crystallises from its solution in methyl alcohol on the addition of water in needles melting at 89—91°:

0.2472 gave 6.9 c.c. of moist nitrogen at 19° and 750 mm.  $\text{N} = 3.17$ .

$\text{C}_{23}\text{H}_{28}\text{O}_5\text{NP}$  requires  $\text{N} = 3.27$  per cent.

The *p*-toluidine salt,  $\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_3 \cdot \text{C}_7\text{H}_7$ , crystallises in a similar manner and melts at 104—106°:

0.1926 gave 5.2 c.c. of moist nitrogen at 18° and 752 mm.  $\text{N} = 3.09$ .

$\text{C}_{24}\text{H}_{30}\text{O}_5\text{NP}$  requires  $\text{N} = 3.17$  per cent.

*Bisdi-p-tolyloxyisopropyl Phosphite*,  $[\text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O}]_2 \cdot \text{PHO}$ .

A mixture of 9.1 grams of *s*-glycerol di-*p*-tolyl ether (2 mols.) was heated in a water-bath with 2.3 grams of phosphorus trichloride (1 mol.) until reaction ceased; the oily product was then dissolved in ether and the ethereal solution shaken with ammonia in order to remove any acid ester which had been formed. The ethereal solution soon deposited the bisdi-*p*-tolyloxyisopropyl phosphite as a crystalline powder, which separated from alcohol in small, transparent plates melting at 81—82°. The yield was 4.3 grams, or about 45 per cent. of the calculated amount:

0.4383 gave 0.0822  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{P} = 5.22$ .

$\text{C}_{34}\text{H}_{39}\text{O}_7\text{P}$  requires  $\text{P} = 5.25$  per cent.

The ester dissolves very easily in ethyl acetate or hot alcohol, and is also soluble in boiling light petroleum.

*Salts of Di-p-tolyloxyisopropylphosphorous Acid,*  
 $\text{CH}(\text{CH}_3 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PHO}(\text{OH}).$

The *aniline* salt,  $\text{CH}(\text{CH}_3 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5$ , crystallises from dilute alcohol in needles melting at  $123-124^\circ$ :

0.2285 gave 0.0599  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{P} = 7.30$ .

$\text{C}_{23}\text{H}_{25}\text{O}_5\text{NP}$  requires  $\text{P} = 7.22$  per cent.

The *p-toluidine* salt,  $\text{CH}(\text{CH}_3 \cdot \text{O} \cdot \text{C}_7\text{H}_7)_2 \cdot \text{O} \cdot \text{PHO} \cdot \text{O} \cdot \text{NH}_2 \cdot \text{C}_7\text{H}_7$ , crystallises similarly and melts at  $144-145^\circ$ :

0.1880 gave 0.0474  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{P} = 7.02$ .

$\text{C}_{24}\text{H}_{30}\text{O}_5\text{NP}$  requires  $\text{P} = 6.99$  per cent.

In conclusion, the author desires to express his thanks to Mr. H. D. Perkins, who prepared and analysed some of the salts described in this paper. The expense of the investigation has been defrayed by a Grant from the Research Fund of the Chemical Society.

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## CXII.—Attempts to Prepare Isomeric Quaternary Salts.

By MARMADUKE BARROWCLIFF and FREDERIC STANLEY KIPPING.

IN a communication to this Society (Trans., 1897, 71, 522), Miss C. de Brereton Evans described the results of some attempts to prepare isomeric ethylpropylpiperidinium iodides. One and the same product was obtained by combining on the one hand ethylpiperidine with propyl iodide, and on the other propylpiperidine with ethyl iodide, but when the compound prepared by either of these methods was crystallised, a mixture was obtained of enantiomorphous, crystals exhibiting optical activity; when separated and dissolved in water, however, each kind of crystal gave an optically inactive solution. It was also found that by dissolving the crystals of either form and recrystallising, a mixture of both was obtained.

As it seemed possible that the absence of optical activity in solution was due to the salt completely racemising, as is the case with Wedekind's phenylbenzylmethylallylammonium iodide (Pope and Harvey, Trans., 1901, 79, 831), the authors have endeavoured to isolate isomeric derivatives from the iodide described by Miss Evans. For this pur-

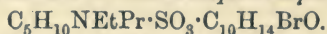


pose, the dextrobromocamphorsulphonate was prepared from the iodide and fractionally crystallised from non-dissociating solvents, but without obtaining the slightest indication of the presence of isomerides. Benzylmethylpiperidinium *d*-bromocamphorsulphonate and ethylpiperidine *d*-bromocamphorsulphonate were examined, but in these cases also, evidence of the existence of more than one form was not forthcoming.

It may be here remarked that the phenomenon noticed by Miss Evans has not been observed in the case of other piperidinium derivatives, and Wedekind found no crystallographic differences on examining benzylallylpiperidinium iodide and benzylpiperidinium iodide ethyl acetate (*Ber.*, 1902, 35, 620). Experiments were next made to try and ascertain whether these quaternary compounds dissociate in solution, because if they do so the absence of isomerism would easily be accounted for, as each isomeride would give the same enantiomorphous mixture. The results, however, seem to show conclusively that dissociation does not occur and hence the failure to obtain isomerides in this class of compounds cannot readily be explained.

#### EXPERIMENTAL.

##### *Ethylpropylpiperidinium d-Bromocamphorsulphonate,*



Ethylpropylpiperidinium iodide, prepared by combining ethylpiperidine with propyl iodide in the manner recommended by Miss Evans, was purified by recrystallisation from acetone, dissolved in alcohol, and treated with an alcoholic solution containing the calculated quantity of silver *d*-bromocamphorsulphonate. After filtering off the silver iodide, the solution was evaporated, when a gummy mass was obtained, which slowly crystallised, and was then evaporated several times with ethyl acetate to free it from alcohol.

The ethylpropylpiperidinium *d*-bromocamphorsulphonate thus obtained is very soluble in water, alcohol, and chloroform, rather less soluble in acetone, sparingly so in ethyl acetate, and insoluble in ether, light petroleum, benzene, and other hydrocarbons. It crystallises from all solvents in needles melting at 211°.

##### *Fractional Crystallisation of Ethylpropylpiperidinium d-Bromocamphorsulphonate.*

(a) *From Alcohol and Ethyl Acetate.*—The substance was dissolved in warm alcohol and sufficient ethyl acetate added; on cooling, the salt crystallised out slowly in needles. Seven fractionations carried out in this manner failed to produce any alteration in the melting points of the first and last fractions, both of which melted at 211°.

The molecular rotation of the first fraction was then found to be  $[M]_D + 272^\circ$ , a value identical with that of *d*-bromocamphorsulphonic acid.

(b) *From Acetone and Ethyl Acetate*.—The salt was dissolved in a small quantity of cold acetone and some ethyl acetate added; the crystals, which soon separated, were fractionally crystallised eight or nine times in this manner without any alteration in melting point being observed. The molecular rotation of the first fraction was then  $[M]_D + 271.6^\circ$ .

(c) *From Chloroform, Petroleum, and Ethyl Acetate*.—The salt was next crystallised from non-dissociating solvents, the use of alcohol and acetone being avoided; its solution in the smallest possible quantity of chloroform, when treated with light petroleum and a small quantity of ethyl acetate, slowly deposited crystals, the properties of which remained unchanged even when this treatment was repeated seven times.

Crystallisation from hot solvents was then employed, the solution of the salt in a small quantity of chloroform was boiled, light petroleum and ethyl acetate were added, and the boiling continued until crystals slowly separated. These processes were repeated six times without changing the melting point. The molecular rotation of the first fraction was then found to be  $[M]_D + 269^\circ$ . Similar experiments with hot acetone and ethyl acetate also gave negative results.

We next tried whether a resolution could be effected at still higher temperatures than those attained in the previous experiments. A few grams of the salt were boiled with xylene, and sufficient amyl alcohol to dissolve about 1/10th of the substance was added. After boiling for some time, the liquid was decanted and the solvent distilled. The residue melted at  $212^\circ$ , and its molecular rotation was found to be  $[M]_D + 270^\circ$ .

To see whether the presence of an optically active substance in solution would aid the resolution, the salt was fractionally crystallised several times from a solution of one part of camphor in two parts of ethyl acetate, but without effect.

*Benzylmethylpiperidinium d-Bromocamphorsulphonate,*  
 $C_5H_{10}NMeBz \cdot SO_3 \cdot C_{10}H_{14}BrO$ .

As it seemed probable that isomerides, if they existed, would be more readily separated if the molecule contained two very dissimilar radicles, such as benzyl and methyl, in the place of ethyl and propyl, and as also the large molecular weight of the benzyl group might prevent it from changing places with any of the other groups, some derivatives of benzylmethylpiperidine were next examined.

Benzylpiperidine, when prepared in the usual manner, purified by fractional distillation, and treated with methyl iodide, yielded a

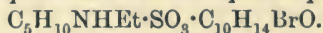


quaternary iodide melting at  $144^{\circ}$ ; this product, which was purified by dissolving in alcohol and precipitating with ether, was then allowed to interact with silver *d*-bromocamphorsulphonate in dilute alcoholic solution. On evaporating off the solvent, a gummy mass remained, which slowly crystallised on cooling. The crystals of benzylmethylpiperidinium *d*-bromocamphorsulphonate melted at  $82-83^{\circ}$ , but after having been heated at  $100^{\circ}$  for some time, the melting point of the salt rose to  $160^{\circ}$ . This salt was fractionally crystallised eight times from its hot solution in chloroform, light petroleum, and ethyl acetate, but the melting points of the first and last fractions were practically identical, and the molecular rotation of the last was found to be  $[M]_D + 270.2^{\circ}$ .

Several grams of the salt were then boiled with a mixture of benzene, light petroleum, and sufficient acetone to bring a small quantity into solution. After boiling for about half an hour, the liquid was decanted and evaporated, when the solid residue melted at  $157^{\circ}$ .

These operations were repeated until only a small portion was left in the flask; the molecular rotation of this residue was found to be  $[M]_D + 270.5^{\circ}$ .

*Ethylpiperidine d-bromocamphorsulphonate.*



This salt was next examined; its solubilities are of the same order as those of the salts previously described; it separates in needles melting at  $158^{\circ}$ . From acetone, it was fractionally crystallised six times, and ten times from its hot solution in acetone, light petroleum, and ethyl acetate, but no change in melting point or specific rotation was observed, and the molecular rotation of the last fraction was found to be  $[M]_D + 272^{\circ}$ .

The salt of ethylpiperidine with Reychler's camphorsulphonic acid, which was also prepared, was hygroscopic and did not crystallise well, and was therefore not further examined.

Unless it is assumed that the salts described above are really mixtures of isomerides, it would seem that in order to account for the negative results of the preceding experiments one of two views may be adopted: (a) that the positions of the three uncombined nitrogen valencies in the group  $C_5H_{10}:N<$  are interchangeable owing to the possibility of rotation, or (b) that the radicles which become attached to these valencies are interchangeable to such an extent that although the positions of the three valencies are fixed, one and the same configuration results in whatever order the groups are introduced.



The latter alternative was experimentally investigated as far as possible, and in the first place we attempted to ascertain whether ethylpropylpiperidinium iodide undergoes dissociation or decomposition in chloroform solution; for this purpose, the following molecular weight determinations were made :

*Ethylpropylpiperidinium Iodide.* M. W. = 282.5.

| Substance.      | Chloroform. | Percentage<br>of salt. | E.    | M. W. |
|-----------------|-------------|------------------------|-------|-------|
| (a) 0.2373 gram | 33 grams    | 0.72                   | 0.049 | 536   |
| 0.5254 "        | "           | 1.60                   | 0.091 | 643   |
| 0.8287 "        | "           | 2.51                   | 0.103 | 790   |
| (b) 0.3008 "    | 32 grams    | 0.94                   | 0.060 | 573   |
| (c) 0.3368 "    | 46.5 "      | 0.72                   | 0.050 | 530   |

To account for these abnormal values, it must be assumed, either that the substance is associated in chloroform solution, or else that it is dissociated and that the products of dissociation vaporise.

When, however, an aqueous solution of the iodide is boiled, no evolution of base or of alkyl iodide can be detected, and the distillate is free from halogen compound; further, on distilling the solution in chloroform, the distillate gives no precipitate with alcoholic silver nitrate solution.

Now if the compound actually underwent dissociation, but to such a very slight extent that the results of the molecular weight determination were not appreciably affected, it should be possible to replace one of the alkyl groups to a greater or less extent by treating the salt with an alkyl halide containing a different hydrocarbon residue to either of those already in the molecule. This should cause a change in the melting point of the salt.

A quantity of the quaternary iodide was shaken with benzyl chloride or methyl iodide and the mixture kept during eight days, but in neither case was any alteration of the melting point to be noticed. These experiments were repeated with the addition of sufficient chloroform to bring the whole of the salt into solution; after some days, the solvent was evaporated, but the melting point of the residue had not been affected.

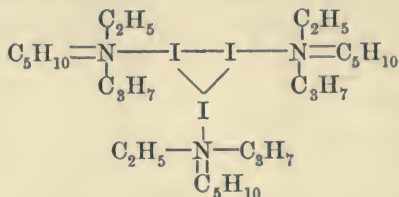
A solution of the iodide in chloroform was mixed with methyl iodide and boiled under a reflux condenser for eight hours, but the melting point of the solid obtained by precipitation with ligroin was the same as that of the salt originally taken.

The molecular weight of ethylpropylpiperidinium iodide in water

was found to be normal, as shown by the following results. Calculated, M. W. = 282.5 :

| Substance.  | Water.     | Percentage. | E.    | M. W. |
|-------------|------------|-------------|-------|-------|
| 0.2106 gram | 20.8 grams | 1.01        | 0.042 | 126   |
| 0.4300 „    | 20.8 „     | 2.06        | 0.079 | 136   |

The abnormal values in chloroform solution are therefore to be ascribed to association, and it seems reasonable to suppose that this is due to the polyvalency of the iodine atom, which may give rise to trimolecular complexes such as



This appears to be the first case of the kind which has been observed.

Wedekind (*Ber.*, 1902, 35, 766) found the molecular weight of phenylbenzylmethylallylammonium iodide in aqueous solution to vary from 343 to 516 with increase of concentration from  $1\frac{1}{2}$  to  $10\frac{1}{2}$  per cent. (calculated value 379.5), but the abnormally high value in this case was proved to be due to the separation and vaporisation of benzyl iodide, which appeared as drops in the tube of the condenser.

Another phenomenon worthy of mention in connection with these experiments is the slowness of the combination of ethylpiperidine with propyl iodide. This reaction was generally carried out by heating together calculated quantities of each reagent on the water-bath for 4—5 hours; the yield was never much greater than 50 percent. of the theoretical. In other experiments, weighed quantities of each reagent were thoroughly mixed in a stoppered bottle and allowed to remain at the ordinary temperature for a month; ether was then added, and the solid collected and thoroughly washed with ether. The yield was 58 per cent., but on allowing the filtrate to remain for another week a further quantity of iodide was obtained, increasing the proportion to 65 per cent., whilst additional amounts of the salt were subsequently deposited from the mother liquor.

The authors beg to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for financial assistance in carrying out this work.

CXIII.—*Some Salts of d- and l- $\alpha$ -Phenylethylamines.*

By ALBERT EDWARD HUNTER and FREDERIC STANLEY KIPPING.

DURING the investigation of the salts of hydrindamine and of methylhydrindamine (this vol., p. 873 *et seq.*), we were led to examine those of several other optically active and *dl*-bases, and amongst these some salts of *dl*- $\alpha$ -phenylethylamine.

This base is easily prepared by the reduction of acetophenone oxime and has been resolved into its *d*- and *l*-components by Loven (*Ber.*, 1896, 29, 2313);\* as the method which he employed was not a very satisfactory one, we tried fractionally crystallising the *d*-bromocamphorsulphonate of the *dl*-base, and in the first place isolated a salt melting at about 206—207°.

Although in dilute aqueous solution the molecular rotation of this salt is  $[M]_D + 271^\circ$  (which is identical with that of the acid), the salt is not partially racemic, but is that of the *l*-base, the basic ion having no appreciable activity; the free base, however, in aqueous alcoholic solution is laevorotatory, its specific rotation being  $[\alpha]_D - 25^\circ$ ; this behaviour recalls that of the *d*- and *l*-hydrindamines (compare Kipping, this vol., p. 873). The *d*-bromocamphorsulphonate of the *d*-base, which remains in the mother liquors from the preceding compound, was only obtained in an impure condition.

When pure *l*-phenylethylamine *d*-bromocamphorsulphonate was decomposed with barium hydroxide and regenerated from its component acid and base, the original salt was recovered apparently unchanged, showing that the base does not racemise under these conditions; when, further, this regenerated salt was repeatedly and systematically crystallised from water, it was not resolved into fractions having appreciably different specific rotations, a result which seems to show that the optically active  $\alpha$ -phenylethylamine does not give rise to separable isomeric salts such as are obtained from hydrindamine.

Similar experiments were made with the *d*-chlorocamphorsulphonate of the *l*-base, but here also systematic crystallisation of the regenerated salt failed to reveal the existence of isomerides, the first and last fractions having practically the same specific rotation.

The salts obtained by combining the *dl*-base and the *l*-base respectively with Reychler's *d*-camphorsulphonic acid were also prepared, and it is interesting to note that the two substances differ very little

\* Having gathered from a recent communication (Thomé, *Ber.*, 1903, 36, 582) that Loven was continuing his work on this compound, and had already published further results in journals which were not accessible to us, we communicated with him, and found that we were working on different lines.



in melting point and have practically the same specific rotation, the data being as follows :

|   | m. p.    | $[\alpha]_D$ | $[M]_D$ |
|---|----------|--------------|---------|
| <i>dl</i> -Phenylethylamine <i>d</i> -bromocamphor-sulphonate ..... | 141—144° | +14.6°       | +51.5°  |
| <i>l</i> -Phenylethylamine <i>d</i> -bromocamphor-sulphonate .....  | 149—150  | 14           | 50      |

Obviously, in this case, it would be barely possible to distinguish between the two salts by optical examination alone.

The benzoyl derivative prepared from the *l*-base is optically inactive, probably owing to racemisation having occurred.

#### *Resolution of dl- $\alpha$ -Phenylethylamine.*

$\alpha$ -Phenylethylamine, prepared by reducing acetophenoneoxime with sodium amalgam and acetic acid in dilute alcohol, is neutralised with an aqueous solution of *d*-bromocamphorsulphonic acid and the solution concentrated; the first and several subsequent deposits consist of compact prismatic crystals, but when about 40 per cent. of the total salt has been separated, the solution yields long, feathery needles, very different in character from the crystals previously obtained. The first deposits, when crystallised several times from water, give long, well-defined, anhydrous prisms, which are only sparingly soluble in water, and which melt sharply at 206—207°; the feathery needles, when fractionally crystallised, yield further quantities of the sparingly soluble salt, which it is extremely difficult, if not impossible, to separate entirely. A sample of the readily soluble salt, which had been fractionally crystallised some 20 or 30 times, melted indefinitely at about 80° when dried on porous earthenware, and appeared to contain water of crystallisation; when dried at 60° for several hours, it melted at about 160°.

Samples of the two salts, dried at 100°, were examined optically in a 200 mm. tube with the following results :

| Salt, m. p.                    | $\alpha_D$ | $[\alpha]_D$ | $[M]_D$ |
|--------------------------------|------------|--------------|---------|
| 206° 0.5 gram 20 c.c. of water | +3.14°     | +62.8°       | +271°   |
| 160° 0.5 " 25 " "              | 2.45       | 61.2         | 264     |

The molecular rotation of *d*-bromocamphorsulphonic acid being +270°, it seemed probable that both these salts were partially racemic, and this view was apparently confirmed by the fact that the benzoyl derivatives of the bases from each of the salts, prepared by the Schotten-Baumann method, were identical in melting point and outward properties with the derivative obtained from the original *dl*-base; mixtures of the three compounds also melted at the same temperature as the single substance, namely, at 120°.

When, however, a small quantity of the pure, sparingly soluble salt was decomposed with barium hydroxide, the liberated base distilled in steam, and combined again with the acid recovered from the barium salt, the product was found to consist entirely of the salt melting at 206—207°; the readily soluble salt, when regenerated in a similar manner, was also unchanged.

Now, if these salts represented isomeric, partially racemic compounds, such as are obtained from hydrindamine, each should have given a mixture of the two isomerides; as this was not the case, we concluded that, in spite of their apparently anomalous molecular rotations, they were really the salts of the two enantiomorphously related bases.

This view was confirmed by decomposing with barium hydroxide a sample of the pure sparingly soluble salt (m. p. 206—207°) having a specific rotation  $[\alpha]_D + 63.2^\circ$ ; the liberated base was distilled in steam and the distillate neutralised with hydrochloric acid; the hydrochloride which was ultimately obtained from the solution was recrystallised from water and from ethyl acetate and dried at 100°.

One gram of this salt, when dissolved in water and the solution diluted to 25 c.c., was examined in a 200 mm. tube and gave  $\alpha_D - 0.3^\circ$ , whence  $[\alpha]_D - 3.7^\circ$ .

As the base appeared to have only a very small specific rotation in solutions of its salts, 1 gram of the hydrochloride was decomposed with caustic potash and the liberated base distilled in steam; the first 25 c.c. of the distillate, when clarified by the addition of alcohol and examined in a 200 mm. tube, gave  $\alpha_D - 1.33^\circ$ , so that the specific rotation  $[\alpha]_D$  of the free base is at least  $-22^\circ$ .

Other determinations in which the quantity of base in the solution was subsequently estimated by titration gave  $[\alpha]_D - 25^\circ$ ; there is therefore no doubt that fractional crystallisation of the *d*-bromocamphorsulphonate of *dl*- $\alpha$ -phenylethylamine effects a resolution into the salts of the *d*- and *l*-bases.

The salt of the *l*-base is readily soluble in hot water, alcohol, and chloroform, sparingly so in cold water, acetone, and carbon tetrachloride, and practically insoluble in ethyl acetate; the salt of the *d*-base is very soluble in cold water and many organic solvents, but only sparingly so in ethyl acetate.

#### *Regeneration of l- $\alpha$ -Phenylethylamine d-Bromocamphorsulphonate.*

It has already been stated that the regenerated *l*- $\alpha$ -phenylethylamine *d*-bromocamphorsulphonate is free from the salt of the *d*-base, and is apparently identical with the original substance. In order to try to isolate isomeric salts such as are obtained from hydrindamine and

from methylhydrindamine (*loc. cit.*), a considerable quantity of the pure salt melting at  $206\text{--}207^\circ$  was decomposed and regenerated from the same acid and the same base.

Although the salt thus obtained was subjected to a prolonged process of fractional crystallisation, the most readily soluble portion, which at first melted at about  $202^\circ$ , when crystallised twice from water melted at  $206^\circ$ , and appeared to be identical with the most sparingly soluble fraction.

As hydrolytic dissociation might possibly account for the failure to isolate isomeric compounds, a second experiment was made, the regenerated salt being fractionally crystallised from a mixture of absolute alcohol and ethyl acetate; the result, however, was the same as before, the first and last fractions differed in melting point by barely  $1^\circ$ , and they had the same specific rotation, namely,  $[\alpha]_D + 50^\circ$  in a 3 per cent. chloroform solution.

#### *l*- $\alpha$ -Phenylethylamine *d*-Chlorocamphorsulphonate.

A solution of the *l*-base prepared from pure *l*- $\alpha$ -phenylethylamine *d*-bromocamphorsulphonate was neutralised with *d*-chlorocamphorsulphonic acid and evaporated; the first deposit, which consisted of long, slender needles, was then recrystallised several times from hot water, in which it was readily soluble; the most sparingly soluble fraction, which then melted at about  $198^\circ$ , was dried at  $100^\circ$  and examined optically.

0.5 gram dissolved in water, the solution diluted to 20 c.c., and examined in a 200 mm. tube, gave  $\alpha_D + 2.4^\circ$ , whence  $[\alpha]_D + 48^\circ$ , and  $[M]_D + 186^\circ$ .

The molecular rotation for *d*-chlorocamphorsulphonic acid being  $[M]_D + 188^\circ$ , this result agrees with those obtained in the determinations made with the *d*-bromocamphorsulphonate in showing that the basic ion is practically devoid of optical activity. The whole of the *d*-chlorocamphorsulphonate was next submitted to fractional crystallisation, and after some 20—30 operations a small quantity of salt was obtained from the last mother liquors; this melted a few degrees lower than the first fraction, but when examined optically it gave the following result, which is practically the same as that obtained with the sparingly soluble fraction referred to above:

0.143 gram dissolved in water, the solution diluted to 20 c.c., and examined in a 200 mm. tube, gave  $\alpha_D + 0.68^\circ$ , whence  $[\alpha]_D + 47.5^\circ$ , and  $[M]_D + 184^\circ$ .

Further fractional crystallisation failed to afford any indication of the presence of isomeric salts, the values finally obtained for the first and last fractions being  $[\alpha]_D + 185.5^\circ$  and  $188^\circ$  respectively in aqueous solution.



*Salts with Reyhler's d-Camphorsulphonic Acid.*

As the *d*-bromocamphorsulphonate of the *d*-base could not be completely separated from the salt of the *l*-base on account of its greater solubility in water, we attempted to prepare the pure *d*-base with the aid of Reyhler's *d*-camphorsulphonic acid. Pope and Harvey (Trans., 1899, 75, 1110) describe the salt of the inactive base as crystallising from acetone in plates melting at 141—143°, and classify it as a partially racemic compound; on repeating the work, our results appeared to agree with theirs, but the melting point of the salt of the *dl*-base was found to be raised several degrees by prolonged crystallisation.

The impure *d*-base obtained from the crude *d*-bromocamphorsulphonate was combined with Reyhler's acid and the salt fractionally crystallised both from acetone and from ethyl acetate; the melting point rose slowly on repeated crystallisation from about 140° to 146°, and the specific rotation of a sample of the salt was then determined.

One gram dissolved in water and the solution diluted to 20 c.c. gave, in a 200 mm. tube,  $\alpha_D + 1.46^\circ$ , whence  $[\alpha]_D + 14.6^\circ$  and  $[M]_D + 51.5^\circ$ .

The molecular rotation for salts of Reyhler's acid with inactive bases being  $[M]_D + 51^\circ$ , this result seemed to indicate the presence of *dl*-base, but bearing in mind the behaviour of *l*- $\alpha$ -phenylethylamine *d*-bromocamphorsulphonate, it was quite possible that the salt was that of the *d*-base; as a matter of fact, the base obtained from this salt was found to have a specific rotation of about  $[\alpha]_D + 8^\circ$ , showing that the preparation consisted of very unequal quantities of the salts of the *d*- and *l*-bases. The salt was therefore crystallised again several times, but although the melting point eventually reached 149° the specific rotation of the base contained in it remained practically the same as before; the base liberated from the most readily soluble fraction had also approximately the same specific rotation as that obtained from the most sparingly soluble portion.

In order to compare the physical properties of the salt of the *l*-base with that of the *dl*-compound, the Reyhler salt was prepared from the pure *l*-base; when crystallised from ethyl acetate several times, it was obtained in plates which were, as far as could be ascertained, identical in appearance with the crystals of the corresponding salt of the *dl*-base and melted at 149—150°.

Optical examination gave the following result: 0.22 gram dissolved in water and the solution diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha_D + 0.31^\circ$ , whence  $[\alpha]_D + 14^\circ$  and  $[M]_D + 50^\circ$ .

These experiments show that the salts of the two enantiomorphously

related bases differ but little from each other and from the salt of the *dl*-base both in solubility and in melting point, so that Reychler's acid is useless for the resolution of the *dl*-base. Whether the salt of the *dl*-base is partially racemic or a mere mixture, there is insufficient evidence to decide.

*Benzoyl Derivative from the l-Base.*

As the benzoyl derivatives prepared from the *d*- and from the *dl*-base respectively melted, as already mentioned, at the same temperature, it seemed desirable to ascertain if the base had undergone racemisation during benzoylation. For this purpose, a small quantity of the pure *d*-chlorocamphorsulphonate was shaken up with strong caustic soda solution and benzoyl chloride in the usual way, and the resulting product crystallised from dilute alcohol.

A solution of about 1 gram in sufficient alcohol to fill a 200 mm. tube was found, on examination in the polarimeter, to possess no optical activity whatever; and, on subsequent hydrolysis with strong hydrochloric acid, the base recovered was found to have undergone complete racemisation. The base itself seems to be stable, and apparently does not undergo racemisation when heated; a sample of the crude *d*-base, which had been distilled under reduced pressure and subsequently under atmospheric pressure, was still optically active.

It seems, therefore, that the base undergoes racemisation during the preparation of the benzoyl derivative.

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CXIV.— $\beta$ -Bromocinnamic Acids.

By JOHN J. SUDBOROUGH and KENWORTHY J. THOMPSON.

$\beta$ -Bromo- and  $\beta$ -bromo*allo*-cinnamic acids were first obtained by Michael and Brown (*Ber.*, 1886, 19, 1379, and 1887, 20, 550) by the action of an aqueous solution of hydrogen bromide, saturated at 0°, on phenylpropionic acid. The two acids were separated by crystallisation first from alcohol and then from chloroform. The  $\beta$ -bromo*allo*-cinnamic acid crystallises from alcohol in extremely well-developed prismatic plates melting at 159—160°, and the  $\beta$ -bromocinnamic acid from chloroform in rhombic prisms resembling cubes and melting at 134—135°. These authors state that the  $\beta$ -acid is stable towards cold concentrated alkalis, whereas the isomeric *allo*-acid is transformed into a neutral, oily substance. E. Erlenmeyer (*Ber.*, 1886, 19, 1936) describes two acids produced by the union of hydrogen bromide with phenylpropionic acid, the one melting at 153·5° and the other at 159—160°. It is highly probable that the former is a mixture of  $\beta$ -bromo*allocinnamic* acid with a small amount of the  $\beta$ -bromo-acid melting at 134—135°.

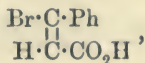
Liebermann and Scholz (*Ber.*, 1892, 25, 950) reduced the  $\beta$ -bromo-*allo*-acid melting at 159—160° with zinc and alcohol and obtained *allocinnamic* acid, thus proving that the less fusible acid was a derivative of *allocinnamic* acid. From its method of formation and from the fact that on oxidation with cold permanganate it does not yield benzaldehyde, they conclude that the bromine atom must be in the  $\beta$ -position with respect to the carboxyl group. These chemists state that they were unable to obtain Michael and Brown's  $\beta$ -bromo-acid melting at 134—135°.

Erlenmeyer (*Annalen*, 1895, 287, 1) confirms Michael and Brown's description of the two  $\beta$ -bromo-acids melting respectively at 159—160° and 134—135°. Sudborough and Lloyd (*Trans.*, 1898, 74, 87) have also prepared the two acids and, from the readiness with which these isomerides may be obtained, find it difficult to account for the negative results first obtained by Erlenmeyer and by Liebermann and Scholz.

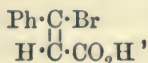
The present investigation was undertaken with the object of studying the reaction between phenylpropionic acid and hydrogen bromide in order to determine whether the two acids are always produced, or whether, under certain conditions, the  $\beta$ -bromo*allocinnamic* acid is the only product. The usual stereochemical conceptions of the phenyl-



propionic acid molecule readily account for the production of the *allo*-acid,



by the addition of hydrogen bromide, and the formation of the  $\beta$ -acid,



must be attributed to intramolecular change.

The investigations of J. Wislicenus (*Annalen*, 1892, 272, 1; 1893, 274, 99, and *Ber.*, 1896, 29, *Ref.* 1080) and Fittig (*Annalen*, 1892, 273, 127) on the addition of bromine to unsaturated compounds suggested the study of the influence of light, temperature, and solvent on the nature of the additive products produced.

The existence of a third cinnamic acid, the so-called *isocinnamic acid* described by Liebermann (*Ber.*, 1890, 23, 141), Erlenmeyer (*Annalen*, 1895, 287, 1), and Michael (*Ber.*, 1901, 34, 3640), introduced a theoretical difficulty into the study of this group of compounds, as the usual van't Hoff-Wislicenus conception admits of only two stereoisomeric  $\beta$ -phenylacrylic acids. Michael's results also tended to show that the so-called  $\beta$ -bromo*allo*cinnamic acid melting at 159—160° is in reality a derivative of *isocinnamic acid*, and that the *allocinnamic acid* obtained during its reduction is probably a secondary product produced by the molecular rearrangement of the *iso*-acid. The later work of Liebermann (*Ber.*, 1903, 36, 176) and Michael (*ibid.*, 900), however, indicates that the so-called *isocinnamic acid* is in all probability not a definite chemical compound, but a mixture of *allocinnamic acid* with some other acid, probably *hydrocinnamic acid*.

## EXPERIMENTAL.

### 1. Preparation of Phenylpropionic Acid.

Michael (*Ber.*, 1901, 34, 3648) recommends the preparation of the mixture of  $\alpha$ -bromo- and  $\alpha$ -bromo*allo*-cinnamic acids by the action of dilute aqueous alkali (2.5 mols. for each mol. of acid) on cinnamic acid dibromide and subsequent transformation of the mixture into  $\alpha$ -bromo-acid by heating for a minute just above the melting point. The  $\alpha$ -bromo-acid is then transformed into phenylpropionic acid by heating for 4 hours on the water-bath with 20 per cent. aqueous potassium hydroxide.

Our previous experiments (*Trans.*, 1903, 83, 680) show that the employment of aqueous alkalis with cinnamic acid dibromide tends to

form  $\omega$ -bromocinnamene, especially if the temperature is not carefully regulated, and also that the transformation of the  $\alpha$ -bromo*allo*-acid into the  $\alpha$ -bromo-compound does not take place so readily as is stated by Michael. As the  $\alpha$ -bromo-acid loses the elements of hydrogen bromide much more readily than the  $\alpha$ -bromo*allo*-acid, we have adopted the following method for the preparation of phenylpropionic acid. Cinnamic acid dibromide is shaken in the cold with alcoholic potash (2 equivalents), the alcohol removed by evaporation, and the two  $\alpha$ -bromo-acids separated by the aid of their barium salts (this vol., p. 673). The  $\alpha$ -bromo*allo*-acid is crystallised from a mixture of light petroleum and chloroform, and then transformed into the  $\alpha$ -bromo-acid by heating for 15—20 minutes at 205—210°, the latter being freed from small amounts of unaltered  $\alpha$ -bromo*allo*-acid by conversion into its barium salt and the regenerated acid transformed into phenylpropionic acid by heating for 2 hours on a gently boiling water-bath with 20 per cent. aqueous potassium hydroxide (2.5 mols.). The solution is filtered to remove small amounts of phenylacetylene, acidified with hydrochloric acid, and the precipitated acid, when dry, crystallised from chloroform. The yield is very good, being about 68—70 per cent. of the calculated amount.

For the preparation of large quantities of  $\alpha$ -bromocinnamic acid, we have worked up considerable amounts of cinnamic acid dibromide with alcoholic potash or soda or the corresponding ethoxide, and we have always observed that the melting point of the crude  $\alpha$ -bromo*allo*-acid is relatively low, being about 110—115°. A good yield of the pure acid melting at 120—121° may, however, be obtained after one crystallisation from a mixture of chloroform and light petroleum. When ethyl cinnamate dibromide is decomposed with alcoholic potash and the acids separated by the aid of their barium salts, the crude  $\alpha$ -bromo*allo*-acid almost invariably melts at 118—119°, indicating that it is practically pure. In order to determine the nature of the impurity present in the sample melting at 110—115°, the crude  $\alpha$ -bromo*allo*-acid was first crystallised from a mixture of chloroform and light petroleum, when the pure compound was deposited. The filtrate was evaporated and the residue thus obtained extracted some 5 or 6 times with small amounts of boiling water until the whole was dissolved. The last extracts, when cold, deposited an acid melting at 155—157° which, after crystallisation from benzene, formed silky, prismatic needles melting at 159—160° and in all respects identical with  $\beta$ -bromo*allocinnamic* acid. The amount of  $\beta$ -acid thus obtained is relatively small, being, as a rule, about 0.75 gram from 70 grams of cinnamic acid dibromide.

Several experiments were undertaken in order to determine whether increase of temperature plays any important part in the yield of the



$\beta$ -bromo*allo*-acid. The results indicate that the influence of this change is practically *nil*.

The question as to whether small amounts of  $\beta$ -bromocinnamic acid may not also be formed together with the *allo*-acid by the action of alkalis on cinnamic acid dibromide must still be regarded as open, since the properties of this acid are such as to render the isolation of small amounts from a mixture of  $\alpha$ -bromo-,  $\alpha$ -bromo*allo*-, and  $\beta$ -bromo*allo*-acids extremely difficult.

Attention has already been drawn to the fact that the  $\alpha$ -bromo*allo*-acid obtained by the action of alkalis on the esters of cinnamic acid dibromide was purer and had a higher melting point (118—119°) than the acid obtained when cinnamic acid dibromide was used. This result seems to indicate that  $\beta$ -bromo*allo*-acid is not produced when an ester is employed in place of the free acid. To test this experimentally, we carried out the following experiment: 60 grams of methyl cinnamate dibromide were added to alcoholic potash (2 mols.) in the cold, the mixture was kept for 3 hours with occasional shaking, the alcohol was removed by evaporation on the water-bath, and the  $\alpha$ -bromo*allo*-acid isolated in the usual manner. The crude acid melted at 117—119°, and when treated in the manner described above gave no trace of  $\beta$ -bromo*allo*-acid. The fact that none of this compound is produced when an ester is employed in place of the free acid dibromide confirms the conclusion previously drawn (*Trans.*, 1903, 83, 678), that in the action of alkalis on the esters the elimination of hydrogen bromide occurs before, and not after, hydrolysis.

## 2. *Separation and Estimation of $\beta$ -Bromo- and $\beta$ -Bromo*allo*-cinnamic Acids and of their Esters.*

As the product obtained by the addition of hydrogen bromide to phenylpropionic acid is a mixture of the two  $\beta$ -acids, it became necessary to find some simple and convenient method of separating them. Michael and Brown first employed a method of fractional separation from alcohol and then from chloroform; they afterwards (*Ber.*, 1887, 20, 552) recommended the precipitation of the  $\beta$ -bromo-acid as its sparingly soluble barium salt. We tried the latter method and found that the  $\beta$ -bromo-acid could readily be obtained pure, but that the  $\beta$ -bromo*allo*-acid always contained small amounts of the  $\beta$ -bromo-acid mixed with it, on account of the fact that barium  $\beta$ -bromocinnamate is sparingly soluble in water at the ordinary temperature. The salts of the acids with either inorganic or organic bases (for example, benzylamine, dimethylaniline, propylamine) were valueless as regards the complete separation of the two acids.

The method ultimately adopted was as follows: 10 grams of the



finely divided phenylpropionic acid were gradually added to the aqueous solution of hydrogen bromide under the conditions specified (p. 1158) in the separate experiments, and the mixture kept for several hours. The product was poured into water and washed; ammonia solution was added, followed by excess of 10 per cent. barium chloride solution, the precipitated barium salt being removed after an interval of one hour. The acid liberated by the addition of hydrochloric acid invariably melted at  $132\text{--}134^\circ$ , and was pure  $\beta$ -bromocinnamic acid. The filtrate from the insoluble barium salt was also acidified with hydrochloric acid, the acid thus obtained melted at  $147\text{--}153^\circ$  and was mainly  $\beta$ -bromo*allo*cinnamic acid mixed with a small amount of the  $\beta$ -bromo-acid. The amount of this admixed acid was estimated in one or two cases. The mixture was crystallised from alcohol, in which the  $\beta$ -bromo*allo*-acid is less soluble, until the last fraction was no longer pure *allo*-acid. The alcohol was removed from the mother liquor and the acids transformed into barium salts, the insoluble barium salt was collected, and the acid liberated. If necessary, the operation was repeated. In one experiment, 0.85 gram of pure  $\beta$ -bromo-acid was obtained from 10 grams of the mixture and in another experiment 1.1 grams. As a rule, it may be said that the mixture contained about 10 per cent. of  $\beta$ -bromo-acid and 90 per cent. of  $\beta$ -bromo*allo*-acid. These results were confirmed by mixing together equal quantities of the two  $\beta$ -acids and separating by means of the barium salts. A mixture containing one gram of each acid when separated in this way gave 0.9 gram of  $\beta$ -bromo-acid melting at  $134\text{--}135^\circ$ , and 1.1 grams of a mixture melting at  $142\text{--}149^\circ$ .

In connection with the experiments on the addition of hydrogen bromide to ethyl phenylpropionate, a method for the estimation of ethyl  $\beta$ -bromocinnamate and of the isomeric *allo*-ester was necessary. We first attempted the hydrolysis of the esters by the aid of alkali and subsequent separation of the two  $\beta$ -acids by means of their barium salts. The results obtained proved that with the ethyl  $\beta$ -bromocinnamate the elimination of hydrogen bromide occurs more readily than hydrolysis, and the product contained phenylpropionic acid and its ester, so that the estimation could not be carried out by the separation of the mixed acid after hydrolysis.

Hydrolysis with sulphuric and hydrobromic acids was very slow and resulted in the formation of oily, neutral substances.

The method ultimately adopted was an indirect one and was based on the fact that the ethyl  $\beta$ -bromocinnamate readily loses hydrogen bromide under the influence of cold dilute alkali, preferably barium hydroxide, whereas the *allo*-ester is merely hydrolysed and loses little or no hydrogen bromide.

Test experiments carried out with known weights of the two esters

proved that the method is fairly accurate: 1.08 gram of ethyl  $\beta$ -bromo-*allo*cinnamate and 1.10 gram of ethyl  $\beta$ -bromocinnamate, both prepared by the Fischer-Speyer method, were mixed and added to a nearly saturated barium hydroxide solution, two equivalents of alkali being employed for each equivalent of ester. Alcohol was added until the ester just dissolved, and the mixture was kept for 20 hours at the ordinary temperature. Care was taken that the temperature did not at any time rise above 16—17°. The mixture was then just acidified with nitric acid and the alcohol evaporated. When cold, an excess of nitric acid was added, the organic acids removed by extraction with ether, and the free hydrobromic acid present in the clear aqueous solution, after evaporating off the ether, was estimated gravimetrically; 0.838 gram of silver bromide was obtained; on the assumption that all the hydrogen bromide comes from the  $\beta$ -bromo-ester and none from the  $\beta$ -bromo*allo*-ester, this gives 1.136 grams of  $\beta$ -ester in place of the 1.1 grams actually taken. In the second experiment, 1.619 grams of  $\beta$ -ester and 1.152 grams of  $\beta$ -*allo*-ester gave 1.2142 grams of silver bromide = 1.646 grams of  $\beta$ -bromo-ester.

The method thus outlined has been employed for the estimation of the amount of  $\beta$ -bromocinnamate present in mixtures; it has been used even when ethyl  $\alpha$ -bromocinnamate was present, as this does not readily lose hydrogen bromide in the presence of cold dilute alkali.

### 3. *Addition of Hydrogen Bromide to Phenylpropionic Acid under Varying Conditions.*

(a.) *Influence of Light and Temperature.*—The presence or absence of sunlight appears to have but little influence on the relative amounts of  $\beta$ -bromo- and  $\beta$ -bromo*allo*-cinnamic acids formed by the union of hydrogen bromide with phenylpropionic acid. The amount of  $\beta$ -bromo-acid melting at 134—135° is very slightly reduced when the addition is carried out completely in the dark.

*Expt. 1.*—Ten grams of finely divided phenylpropionic acid were gradually added to 50 c.c. of hydrobromic acid (sp. gr. 1.78) saturated at 0°. The mixture was kept at 0° during the addition, and was afterwards surrounded by ice for 20 hours although exposed to fairly bright sunlight. The yields were 5.5 and 9.9 grams of  $\beta$ -bromo- and  $\beta$ -bromo*allo*-acids respectively.\*

A number of similar experiments have been made under slightly varying conditions, and the results are given in Table I.

\* These are the numbers for the pure acids, assuming that the mixture from the soluble barium salt contains 10 per cent. of  $\beta$ -bromo-acid and 90 per cent. of  $\beta$ -bromo*allo*-acid.

TABLE I.

| No. of expt. | Weight of acid taken. | Temp. | Light or dark-ness. | Sp. gr. of hydro-bromic acid. | Weight of $\beta$ -bromo-acid. | Weight of $\beta$ -bromo-allo-acid. | Total. |
|--------------|-----------------------|-------|---------------------|-------------------------------|--------------------------------|-------------------------------------|--------|
| 1            | 10 grams              | 0°    | L                   | 1.78 at 0°                    | 5.5                            | 9.9                                 | 15.4   |
| 2            | 10 "                  | 0     | L                   | "                             | 5.3                            | 9.75                                | 15.05  |
| 3            | 10 "                  | 0     | L                   | "                             | 5.7                            | 9.0                                 | 14.7   |
| 4            | 10 "                  | 10    | L                   | "                             | 5.6                            | 8.9                                 | 14.5   |
| 5            | 10 "                  | -8    | L                   | "                             | 5.9                            | 9.0                                 | 14.9   |
| 6            | 5 "                   | 35-45 | L                   | "                             | 2.7                            | 4.7                                 | 7.4    |
| 7            | 10 "                  | 0     | D                   | "                             | 4.9                            | 10.25                               | 15.15  |
| 8            | 10 "                  | -10   | D                   | "                             | 5.0                            | 10.2                                | 15.2   |
| 9            | 10 "                  | 0     | D                   | "                             | 4.7                            | 9.0                                 | 13.7   |
| 10           | 10 "                  | 0     | D                   | "                             | 4.6                            | 9.0                                 | 13.6   |

The theoretical yield of  $\beta$ -bromo-acid from 10 grams of phenylpropionic acid is 15.54 grams. The amounts of acids obtained in experiments 9 and 10 are low, owing to the formation of a small quantity of a neutral, oily substance, which was only noticed in experiments conducted in the dark, and, even under these conditions, in only one or two isolated experiments. The amount obtained was too small to admit of purification and analysis.

(b) *Influence of Concentration.*—No addition occurs unless the hydrobromic acid employed is sufficiently concentrated, for example, experiments carried out at 0° with an acid of sp. gr. 1.65 gave absolutely no  $\beta$ -bromo-acid.

Provided the acid is sufficiently strong to admit of the addition taking place, slight variations in the concentration (from 1.71 to 1.78) do not appreciably affect the relative amounts of the two  $\beta$ -acids produced.

(c) *Influence of the Solvent on the Addition.*—The nature of the medium in which the phenylpropionic acid is suspended or dissolved exerts a much more marked influence on the course of the reaction than any of the other factors mentioned. Not merely are the relative amounts of the two  $\beta$ -bromo-acids affected, but the actual position taken up by the entrant bromine atom may be entirely altered by a change of solvent.

The solvents we have employed in addition to water are alcohol, ether, glacial acetic acid, chloroform, benzene, and carbon disulphide. When water or acetic acid is employed as a solvent, the only products appear to be  $\beta$ -bromo- and  $\beta$ -bromoallo-cinnamic acids, the yield of  $\beta$ -bromo-acid being somewhat larger with the latter solvent. With ether and alcohol, the two  $\beta$ -acids are also formed together with esters,



but no  $\alpha$ -bromo-acid. Benzene and carbon disulphide give rise almost exclusively to  $\alpha$ -bromocinnamic acid melting at  $131^{\circ}$ , and in chloroform solution a mixture of the  $\beta$ -bromo- and  $\beta$ -bromoallo-acids with about 40 per cent. of  $\alpha$ -bromocinnamic acid is obtained. It will be noticed that ionising media tend to favour the production of the  $\beta$ -acids, whilst the use of associating solvents leads to the formation of the  $\alpha$ -bromo-acid.

*Expt. 11.*—Five grams of phenylpropionic acid were added to 50 c.c. of a glacial acetic acid solution of hydrogen bromide, which was obtained by saturating the solvent with the gas at  $0^{\circ}$ , and had a sp. gr. 1.43 at  $0^{\circ}$ . The mixture was exposed to light at  $0^{\circ}$  for several hours, then poured into water, and the precipitated acids removed and separated by means of their barium salts. The total yield of acids (4.2 grams of  $\beta$ -bromo-acid and 2.3 grams of  $\beta$ -bromoallo-acid) was somewhat less than in the previous experiments where aqueous solutions of hydrogen bromide were employed, probably owing to the solubility of these substances in dilute acetic acid. The numbers clearly show that the yield of  $\beta$ -bromo-acid is much greater with acetic acid than with water.

*Expt. 12.*—Five grams of phenylpropionic acid were added to 30 c.c. of benzene (b. p.  $80-85^{\circ}$ ), and a slow current of dry hydrogen bromide was passed in for  $1\frac{1}{4}$  hours at the ordinary temperature and in diffused daylight. The long, silky needles, which were deposited, when washed with benzene and dried, had all the characteristic properties of  $\alpha$ -bromocinnamic acid; they melted at  $129-130^{\circ}$ , gave an insoluble barium salt, and the melting point was not altered by admixture with pure  $\alpha$ -bromo-acid. Hydrogen bromide was passed into the benzene filtrate for another hour, the solvent removed by evaporation, and the residual acids separated by means of their barium salts. An additional 1.9 grams of  $\alpha$ -bromo-acid were thus obtained, together with 0.03 gram of an acid having a soluble barium salt and melting at  $125-130^{\circ}$ .

Several experiments conducted under conditions similar to those of No. 12 gave identical results. The acid from the soluble barium salt proved, on examination, to be  $\beta$ -bromocinnamic acid.

*Expt. 13.*—Five grams of phenylpropionic acid were dissolved in dry chloroform, and dry hydrogen bromide was passed into the solution in diffused daylight for 6 hours at  $17^{\circ}$ . After leaving the mixture overnight in a stoppered flask, the chloroform was evaporated at the ordinary temperature, and the acids separated by means of their barium salts; 5.5 grams of a mixture of  $\alpha$ -bromo- and  $\beta$ -bromocinnamic acids melting at  $115-120^{\circ}$  were obtained together with 1.2 grams of  $\beta$ -bromoallo-acid melting at  $159^{\circ}$ . The mixture of  $\alpha$ - and  $\beta$ -bromocinnamic acids was mixed with an excess of moderately strong

potassium hydroxide solution and kept at the ordinary temperature for several hours. By this means, the  $\beta$ -bromo-acid was transformed into phenylpropionic acid, whilst the  $\alpha$ -bromo-acid was unaffected, and was separated and purified by the aid of its barium salt; 2.65 grams of  $\alpha$ -bromocinnamic acid melting at 129—130° were thus obtained.

*Expt. 14.*—Five grams of finely divided phenylpropionic acid were suspended in 50 c.c. of dry and freshly distilled carbon disulphide and dry hydrogen bromide passed in for 4½ hours. After 2 hours, all the phenylpropionic acid had dissolved, but crystals afterwards separated, the flask being corked and kept overnight at the ordinary temperature. The solvent was then removed and the acid separated in the usual manner.

The insoluble barium salt gave 7.0 grams of pure  $\alpha$ -bromocinnamic acid melting at 130—131°, and the soluble barium salt gave 0.15 gram of a mixture from which a definite acid could not be isolated.

#### 4. Addition of Hydrogen Bromide to Ethyl Phenylpropiolate]

We have already shown (this vol., p. 676) that the presence of an alkyl radicle in place of the hydrogen atom of the carboxyl group in cinnamic acid dibromide affects to a remarkable extent the elimination of hydrogen bromide from the dibromide. This led us to undertake experiments in order to determine whether the substitution of esters of phenylpropionic acid for the free acid would materially affect the nature and relative amounts of the products obtained by the addition of hydrogen bromide.

The results tabulated on p. 1162 show that the alkyl group exerts no disturbing influence on the addition, as in all cases similar products are obtained with either the ester or the free acid. In this case also, the chief factor appears to be the solvent.

The ethyl phenylpropiolate, obtained by the Fischer-Speyer method, distilled at 151—152° under 12—13 mm. pressure as an almost colourless oil.

The amounts of ethyl  $\beta$ -bromocinnamate and of ethyl  $\beta$ -bromoallo-cinnamate were estimated in the mixed products by the method already described.

The general method of procedure in these experiments was as follows: ethyl phenylpropiolate was dissolved in the dry solvent and saturated with dry hydrogen bromide at the ordinary temperature. The solution was left for a few hours in diffused daylight, again saturated with hydrogen bromide, and left overnight in a closed vessel. After removing the solvent, the residue was dissolved in ether, washed several times with water until free from hydrogen bromide, then dried, and the ether removed. The percentage of  $\beta$ -bromo-ester

| No. of expt. | Weight of ethyl phenylpropiolate. | Solvent.         | Weight of brominated ester. | Percentages of         |                       |                            |
|--------------|-----------------------------------|------------------|-----------------------------|------------------------|-----------------------|----------------------------|
|              |                                   |                  |                             | $\alpha$ -Bromo-ester. | $\beta$ -Bromo-ester. | $\beta$ -Bromo-allo-ester. |
| 15           | 5                                 | Absolute alcohol | 7.13                        | 0                      | 56                    | 44                         |
| 16           | 5                                 | "                | 7.1                         | 0                      | 57                    | 43                         |
| 17           | 5                                 | Dry ether        | 7.2                         | 0                      | 62                    | 38                         |
| 18           | 5                                 | "                | 7.2                         | 0                      | 64                    | 36                         |
| 19           | 5                                 | Chloroform       | 7.2                         | 20                     | 60                    | 20                         |
| 20           | 5                                 | "                | 7.2                         | 22.5                   | 55.5                  | 22                         |
| 21           | 5                                 | Dry benzene      | 7.28                        | 70                     | 15.5                  | —                          |
| 22           | 5                                 | "                | 7.2                         | 73                     | 14                    | —                          |

was estimated by taking a given weight of the ester and removing hydrogen bromide by the aid of barium hydroxide in the manner previously described.

The ethyl  $\alpha$ -bromocinnamate, when present, was estimated after hydrolysis by conversion into its insoluble barium salt.

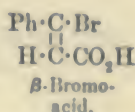
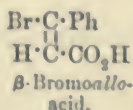
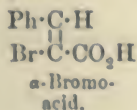
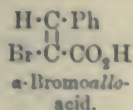
In experiments 21 and 22 the acid obtained after hydrolysis and removal of the  $\alpha$ -bromo-acid consisted of nearly pure phenylpropionic acid obtained from the  $\beta$ -bromo-ester, and hence only very small amounts of the  $\beta$ -bromoallo-ester could have been formed under the given conditions.

#### 5. Action of Alkalis on $\beta$ -Bromo- and $\beta$ -Bromoallo-cinnamic Acids, and their Esters.

Both  $\beta$ -bromo- and  $\beta$ -bromoallo-cinnamic acids and their esters are readily converted into phenylpropionic acid when warmed with dilute solutions of barium, potassium, or sodium hydroxide, but are not attacked by sodium carbonate solution or dilute ammonia. Very concentrated aqueous potassium hydroxide in the cold also converts the acids and their esters into phenylpropionic acid. When cold dilute caustic alkalis are employed, a marked difference is noticed in the readiness with which the two acids and also their esters lose the elements of hydrogen bromide, the  $\beta$ -bromo-acid and its esters being much more readily transformed into phenylpropionic acid than the isomeric  $\beta$ -bromoallo-acid and its esters. This phenomenon is similar to that previously noticed in the case of the  $\alpha$ -bromocinnamic acids. In both cases, the allo-acid, in which, if we assume the usual constitutional formulæ for these acids, the hydrogen and bromine atoms are in adjacent positions, lose hydrogen bromide less readily than the



$\alpha$ - and  $\beta$ -acids, in which the hydrogen and bromine are as far removed from one another as possible.



The acid which is obtained when methyl  $\beta$ -bromocinnamate is left in contact with concentrated aqueous potassium hydroxide for several days and the mixture then acidified has been proved to be phenylpropionic and not  $\beta$ -bromocinnamic acid. The acid described by Sudborough and Lloyd (Trans., 1898, 73, 87) as melting at 133—134° is undoubtedly phenylpropionic acid. When the two isomeric methyl esters are separately warmed with dilute aqueous potassium hydroxide (1 mol.), it is noticed that after the solutions have become neutral a considerable amount of oily ester remains in the case of the  $\beta$ -bromo-ester, indicating that the alkali has been employed in removing hydrogen bromide and not in hydrolysing the esters; with the  $\beta$ -bromoallo-ester, nearly all the oil has disappeared when the solution becomes neutral, indicating that a considerable proportion of the alkali is employed in hydrolysing the ester and not in removing hydrogen bromide. In both cases, the addition of a second equivalent of alkali acid leads, on further warming, to the production of phenylpropionic acid.

Similar results have been obtained by the use of barium hydroxide and dilute alcoholic potash solution.

The action of aqueous barium and potassium hydroxides on the free  $\beta$ -bromo- and  $\beta$ -bromoallo-acids has been studied, and the results, which are exhibited in the four following tables, clearly indicate the different rates at which the elements of hydrogen bromide are removed in the two cases.

The method employed was to dissolve a known weight of the acid in the alkali (2 equivalents) and to titrate the excess of this reagent at given intervals. With the  $\beta$ -bromo-acid and barium hydroxide, the matter is rendered more complex by the slight solubility of the barium salt. In order to make sure that the whole of the acid was transformed into barium salt, a pure crystallised specimen of this salt was mixed with 1 equivalent of dilute barium hydroxide solution. As there was always some undissolved salt present, the concentration of this compound may be considered as constant, and the reaction should therefore be a unimolecular one. In all cases, the solutions were kept in bottles at the ordinary temperature and protected from atmospheric carbon dioxide; 20 c.c. were removed at given intervals and titrated with standard hydrochloric acid.

TABLE III.

Barium  $\beta$ -bromocinnamate (5.3 grams) and 1 equivalent of barium hydroxide solution (about 0.09 normal).

Strength of acid used for titration, 1 c.c. = 0.004137 gram of HCl.

A (initial concentration) = 15.93 c.c. of acid.

| $t$ (in hours). | $A - x$ (in c.c. of acid). | $1/t \log A/A - x$ . |
|-----------------|----------------------------|----------------------|
| 2               | 15.2                       | 0.0102               |
| 4               | 14.4                       | 0.0110               |
| 6               | 13.7                       | 0.0109               |
| 24              | 9.0                        | 0.0103               |
| 48              | 5.2                        | 0.0101               |
| 72              | 3.06                       | 0.0100               |

TABLE IV.

$\beta$ -Bromoallocinnamic acid (5 grams) was dissolved in aqueous barium hydroxide (2 equivalents).

Strength of acid used for titration, 1 c.c. = 0.003201 gram of HCl.

A = 20.2 c.c. of acid.

| $t$ (in days). | $A - x$ . | $x$ . | $1/t \frac{x}{A(A - x)}$ . |
|----------------|-----------|-------|----------------------------|
| 1              | 19.05     | 1.15  | 0.00299                    |
| 2              | 18.30     | 1.90  | 0.00257                    |
| 3              | 17.95     | 2.25  | 0.00207                    |
| 4              | 17.36     | 2.84  | 0.00202                    |
| 6              | 15.52     | 4.68  | 0.00249                    |

TABLE V.

$\beta$ -Bromocinnamic acid (5 grams) and 2 equivalents of potassium hydroxide. A = 15.8 c.c. of acid.

Strength of acid, 1 c.c. = 0.0040923 gram of HCl.

| $t$ (in hours). | $A - x$ . | $x$ . | $1/t \frac{x}{A(A - x)}$ . |
|-----------------|-----------|-------|----------------------------|
| 24              | 6.95      | 8.85  | 0.00336                    |
| 45              | 5.00      | 10.80 | 0.00304                    |
| 79              | 3.70      | 12.10 | 0.00262                    |
| 103.5           | 3.00      | 12.80 | 0.00261                    |

TABLE VI.

$\beta$ -Bromo*allocinnamic* acid (5 grams) and aqueous potassium hydroxide (2 equivalents).

Strength of acid, 1 c.c. = 0.0040023 gram of HCl.

$A = 15.8$  c.c. of acid.

| $t$ (in hours). | $A - x$ . | $x$ . | $1/t \frac{x}{A(A-x)}$ |
|-----------------|-----------|-------|------------------------|
| 24              | 15.3      | 0.5   | 0.0000862              |
| 45              | 14.9      | 0.9   | 0.0000849              |
| 79              | 14.45     | 1.35  | 0.0000750              |
| 103.5           | 14.0      | 1.8   | 0.0000786              |
| 154             | 13.41     | 2.39  | 0.0000732              |
| 202             | 12.73     | 3.07  | 0.0000755              |
| 254             | 12.05     | 3.75  | 0.0000775              |

The last two tables prove that the  $\beta$ -bromo-acid loses hydrogen bromide about 40 times as rapidly as the  $\beta$ -bromo*allo*-acid.

#### 6. Reduction of $\beta$ -Bromo*allocinnamic* Acid and Attempts to prepare Michael's *isoCinnamic* Acid.

The question of the existence of a third cinnamic acid (*isocinnamic* acid) is of immense importance in its bearing on the theory of unsaturated compounds. So far, it is the only example of an olefine compound which has been stated to exist in more than two stereoisomeric modifications. Michael, in his first paper (*Ber.*, 1901, 34, 36), claims to have proved the existence of three well-defined cinnamic acids. One of the chief original objects of this research was the preparation of *isocinnamic* acid and a determination of some of its physical constants, such as its electrical conductivity and esterification constant. The ordinary theory only accounts for two stereoisomeric cinnamic acids, in both of which the constituent groups are supposed to lie in the same plane. The simplest method of accounting for a third isomeric acid is to suppose that the groups ( $H, H, Ph, CO_2H$ ) do not all lie in the same plane. The result would be the complete asymmetry of the molecule and the possibility of the resolution of one of the three cinnamic acids into optically active constituents.

The more recent criticisms of Liebermann (*Ber.*, 1903, 36, 176) and Michael's second communication (*ibid.*, 900) tend to show that the so-called *isocinnamic* acid is probably a mixture of *allocinnamic* and *hydrocinnamic* acids. We have carried out a number of experi-



ments, following Michael's directions as closely as possible, in order to prepare *isocinnamic acid*. We have used both zinc dust and zinc filings, also absolute and 95 per cent. alcohol. The acid obtained by us, when converted into the barium salt and extracted with pure methyl alcohol, gave, on acidification with hydrochloric acid, a solid acid melting at 54—60°, and not an oily acid which slowly solidified and then melted at 36—38°. The acid melting at 54—60° gave an almost theoretical yield of aniline salt melting at 81—82°, and was merely *allocinnamic acid* mixed with a minute quantity of some impurity.

#### 7. Transformation of $\beta$ -Bromoallocinnamic Acid into $\beta$ -Bromocinnamic Acid.

This transformation has been accomplished by the aid of sunlight both in the case of the acid itself and of its barium salt.

Three grams of the finely divided  $\beta$ -bromoallo-acid were exposed between watch-glasses to moderately bright sunlight for 10 weeks. It was noticed that even after a few days the melting point was no longer sharp, at the end of the 10 weeks it began to melt at 124°, and was completely fused at 147°. 0.37 gram of pure  $\beta$ -bromocinnamic acid was separated by the aid of its sparingly soluble barium salt.

Similar results were obtained by exposing a solution of barium  $\beta$ -bromoallocinnamate to sunlight. In the course of 2 or 3 days, crystals of the isomeric, sparingly soluble salt began to separate, and after 6 weeks, 0.2 gram of pure  $\beta$ -bromo-acid was obtained from 1 gram of the allo-acid.

#### 8. Summary.

The more important conclusions to be drawn from the experimental work described in this paper are:

1. Small amounts of  $\beta$ -bromoallocinnamic acid are formed, in addition to the two  $\alpha$ -bromocinnamic acids, by the action of alkali on cinnamic acid dibromide.

2. The  $\beta$ -bromoallo-acid is not produced when an ester is substituted for the free cinnamic acid dibromide.

3.  $\beta$ -Bromo- and  $\beta$ -bromoallo-cinnamic acids cannot be completely separated by the aid of their barium salts, although this appears to be the simplest method of determining the amount of each in a mixture of the two.

4. The relative amounts of  $\beta$ -bromo- and  $\beta$ -bromoallo-cinnamic acids obtained by the addition of hydrogen bromide in aqueous solution are only slightly affected by (a) light, (b) temperature, (c) concentration of the hydrobromic acid.

5. The substitution of other solvents in place of water may not only affect the relative amounts of the two  $\beta$ -acids produced, as, for example, with glacial acetic acid, but may, as in the case of benzene and carbon disulphide, entirely alter the nature of the products, producing an  $\alpha$ - in place of a  $\beta$ -brominated acid.

6. Ethyl phenylpropiolate behaves very similarly to the acid itself.

7. Under the influence of alkalis,  $\beta$ -bromocinnamic acid and its esters lose hydrogen bromide much more rapidly than the  $\beta$ -bromo-*allo*-acid and its esters. When cold potassium hydroxide acts on the acids, the rates of change are in the ratio of 40 : 1.

8. Both acids lose hydrogen bromide more readily than the  $\alpha$ -bromocinnamic acids.

9. Under the influence of sunlight,  $\beta$ -bromo*allocinnamic* acid and its barium salt are partially transformed into the isomeric  $\beta$ -acid and its barium salt respectively.

10. An almost theoretical yield of *allocinnamic* acid may be obtained by the reduction of  $\beta$ -bromo*allocinnamic* acid with zinc and alcohol. Even when 95 per cent. alcohol is employed, no *isocinnamic* acid appears to be formed.

We beg to tender our thanks to the Research Fund Committee of the Chemical Society for the grants which have largely met the expenses incurred in this investigation, and also in that previously carried out on the  $\alpha$ -bromocinnamic acids.

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[Since the above paper was written, my attention has been drawn to a communication by E. Erlenmeyer, jun. (*Ber.*, 1903, **36**, 2340), in which it is stated that the existence of three, or even four, distinct cinnamic acids is explicable, on the assumption that in only two of them are all the radicles in the same plane.

It is suggested that *allocinnamic* acid and  $\beta$ -bromocinnamic acid may be resolvable into optically active constituents.

The experimental work contained in the above, and also in a previous communication (this vol., p. 666), was commenced by Mr. Thompson in December, 1901, with the object of preparing large quantities of the *allo*-acid and Michael's *isocinnamic* acid in order to determine whether either could be resolved by active bases. A considerable amount of the *allo*-acid has been obtained, but, as stated above, no *iso*-acid. In view of the investigations of Michael and Liebermann, the existence of a third acid is very questionable, and hence the possibility of the resolution of one of the two known acids does not appear probable. I hope, however, shortly to attempt to resolve the *allo*-acid and also the  $\alpha$ - and  $\beta$ -bromo*allocinnamic* acids, which are stated by some authorities to yield an *isocinnamic* acid on reduction.—J. J. S.]

## CXV.—*Vapour Pressure of Aqueous Ammonia Solution.* *Part II.*

By EDGAR PHILIP PERMAN.

IN a former paper (Trans., 1901, 79, 718), I have published the results of the determination of the vapour pressure of aqueous ammonia solution for various temperatures and concentrations. For the sake of reference and for comparison with the results obtained by another method, these data have been further elaborated. The values of the vapour pressure for percentage concentrations of 2.5, 5.0, &c., were read off from the original isothermal curves, and the values for each concentration were then plotted against temperature, giving a series of curves which I suggested (Trans., 1902, 81, 483) should be called "isosthens," or lines showing the relation between pressure and temperature for solutions of equal concentration. These curves were continuous, and were drawn without difficulty with the help of a set of curved rulers, or in some cases with a thin steel strip kept in position by a series of projecting brass rods, which could be screwed to a brass framework.

These curves may, without appreciable error, be considered as being straight for a variation in temperature of not more than 2°. The values of vapour pressure have therefore been read off at intervals of 2°, and are arranged in the table on p. 1169.

The horizontal columns give the isothermals, and the vertical columns the isosthens. The values for intermediate temperatures or concentrations can be deduced without serious error by taking proportional parts; if greater accuracy is required, the curves can be constructed from the tabulated numbers. The pressures are given to the nearest half millimetre, which is about the limit of accuracy attained in the measurements.

### *The Partial Vapour Pressures of Aqueous Ammonia Solution.*

IN order to measure the partial pressures of the ammonia and the water vapour given off by an aqueous ammonia solution, it was necessary to devise some method of estimating the quantity of each constituent in the vapour thus evolved; the method which seemed to me the most promising was to aspirate a current of air through the solution and then through suitable absorbents. Before adopting this process, I made some preliminary experiments on pure water, which showed that the vapour pressure of water could in this way be found with great accuracy. I have since made further experiments up to 90° with a similar result (*Proc. Roy. Soc.*, 1903, 72, 72).



## Percentage of Ammonia.

| Temp.                              | 0.    | 2.5   | 5.0   | 7.5   | 10.0  | 12.5  | 15.0  | 17.5  | 20.0  | 22.5  | 25.0  | 27.5  | 30.0  |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Vapour pressure in mm. of mercury. |       |       |       |       |       |       |       |       |       |       |       |       |       |
| 0                                  | 4.5   | 13    | 30    | 37.5  | 35    | 45    | 57    | 75    | 93    | 117   | 144.5 | 181   | 220   |
| 2                                  | 5.5   | 13.5  | 30.5  | 38.5  | 36.5  | 47.5  | 60.5  | 80    | 101   | 126.5 | 158.5 | 198   | 242   |
| 4                                  | 6     | 14    | 31    | 39    | 39    | 51    | 66    | 86.5  | 110   | 137.5 | 174   | 216   | 266   |
| 6                                  | 7.0   | 15    | 32.5  | 39.5  | 43    | 56    | 72.5  | 94.5  | 120   | 150   | 190   | 236   | 291   |
| 8                                  | 8     | 16    | 34.5  | 41    | 48    | 62    | 80    | 104.5 | 131.5 | 164.5 | 207   | 257.5 | 318   |
| 10                                 | 9     | 18    | 37    | 44    | 54    | 69    | 89    | 115   | 144   | 180.5 | 226.5 | 280   | 346   |
| 12                                 | 10.5  | 20    | 39    | 46    | 60    | 77    | 99    | 127   | 159   | 199   | 248.5 | 306   | 377.5 |
| 14                                 | 12    | 22    | 39.5  | 50    | 67    | 85.5  | 110.5 | 140.5 | 176   | 219   | 273   | 335.5 | 412   |
| 16                                 | 13.5  | 23    | 37    | 56    | 75    | 95.5  | 123   | 156   | 194.5 | 241   | 299.5 | 367   | 450   |
| 18                                 | 15.5  | 28.5  | 42    | 62.5  | 84    | 106   | 136.5 | 173   | 215.5 | 265   | 329.5 | 402   | 492   |
| 20                                 | 17.5  | 32.5  | 47.5  | 70    | 93    | 118   | 151   | 191   | 237   | 291   | 360   | 440   | 537   |
| 22                                 | 20    | 36.5  | 53    | 77.5  | 103   | 131   | 167.5 | 210   | 260.5 | 319   | 395.5 | 482   | 586   |
| 24                                 | 22.5  | 41.5  | 59.5  | 85.5  | 114   | 145   | 185.5 | 231.5 | 286   | 349   | 432.5 | 527   | 639   |
| 26                                 | 25    | 46.5  | 66    | 95    | 126   | 160   | 204   | 254.5 | 313   | 382   | 472   | 575.5 | 696.5 |
| 28                                 | 28.5  | 51.5  | 74    | 104.5 | 139   | 176   | 223   | 279   | 342   | 417   | 515.5 | 626   | 754   |
| 30                                 | 31.5  | 56.5  | 83    | 115   | 153.5 | 193.5 | 245   | 305.5 | 373   | 455.5 | 561   | 680   | 817   |
| 32                                 | 35.5  | 62.5  | 92    | 127   | 168.5 | 212.5 | 267.5 | 333.5 | 407.5 | 497   | 609.5 | 738   | 884   |
| 34                                 | 40    | 69    | 102   | 140   | 185   | 233.5 | 292   | 363.5 | 444.5 | 540   | 660   | 800   | 954   |
| 36                                 | 44.5  | 76    | 112   | 153.5 | 202   | 265   | 318   | 395.5 | 483.5 | 587   | 714   | 864.5 | 1027  |
| 38                                 | 49.5  | 83.5  | 122.5 | 167.5 | 221   | 278.5 | 347.5 | 429.5 | 525.5 | 637   | 771   | 931   | 1105  |
| 40                                 | 55    | 91    | 134.5 | 183   | 241   | 303.5 | 377.5 | 465.5 | 569.5 | 690   | 830.5 | 1007  | 1189  |
| 42                                 | 61.5  | 100   | 147.5 | 199   | 263   | 330   | 410   | 504   | 617   | 745   | 894   | 1081  | 1276  |
| 44                                 | 68    | 110   | 161   | 216.5 | 286   | 358   | 444   | 545   | 666   | 804   | 962   | 1157  | 1367  |
| 46                                 | 75.5  | 120   | 175.5 | 256   | 310   | 388   | 481   | 588   | 719.5 | 866.5 | 1034  | 1235  | 1460  |
| 48                                 | 83.5  | 132   | 192   | 257.5 | 336   | 420   | 521.5 | 632.5 | 776   | 933   | 1111  | —     | —     |
| 50                                 | 92.5  | 146   | 210   | 281   | 363.5 | 454   | 564   | 684.5 | 834.5 | 1005  | 1195  | —     | —     |
| 52                                 | 102   | 161   | 230   | 306   | 395   | 491.5 | 609   | 737.5 | 897   | 1080  | —     | —     | —     |
| 54                                 | 112.5 | 177   | 252   | 332   | 427.5 | 530.5 | 656   | 792.5 | 963   | 1159  | —     | —     | —     |
| 56                                 | 123.5 | 194.5 | 275   | 360.5 | 461.5 | 572   | 706   | 852.5 | 1033  | 1242  | —     | —     | —     |
| 58                                 | 136   | 213.5 | 300   | 391   | 498.5 | 617.5 | 759   | 917   | 1109  | 1333  | —     | —     | —     |
| 60                                 | 149.5 | 234   | 327   | 425   | 539   | 666   | 816.5 | 985   | 1191  | 1432  | —     | —     | —     |
| 62                                 | 163.5 | 255.5 | 355   | 460   | 582   | 717   | 878.5 | 1061  | 1279  | —     | —     | —     | —     |

As the method proved satisfactory for water, I employed it for the ammonia solution; in order to estimate both the ammonia and the water, the mixture of air, ammonia, and water vapour was made to pass through dilute sulphuric acid of measured volume and strength, and then through strong sulphuric acid; the total increase in weight gave the weight of ammonia and water carried off by the air current; the weight of ammonia was found by titration, that of the water being obtained by difference.

I have already shown that the air passing through the solution takes up the ammonia and water vapour, and becomes saturated with great rapidity, also that the ammonia is very rapidly absorbed by the dilute acid solution. The air current was always slower than 0.1 litre per minute, and considerably less than this with the more concentrated solutions. The experiments were therefore of a tedious nature, but the method adopted was, in my opinion, the only one practicable.

*Apparatus.*—The apparatus employed was nearly the same as that used in my experiments (*loc. cit.*) on the vapour pressure of water, the chief difference being the introduction of a second absorption

apparatus for the ammonia. This vessel was similar to the one used for the absorption of the water, but was larger, the capacity of the bulbs being about 100 c.c. and 20 c.c. respectively; it was placed between the flasks containing the ammonia solution and the absorption-bulbs for the water. There were only two other essential differences: (1) the last flask, containing the ammonia solution, could be detached from the rest, so that the strength of the solution in it might be estimated; (2) the air was freed from carbon dioxide, before passing into the ammonia solution, by means of a tube of soda-lime.

*Method of Work.*—In general, the procedure was the same as in the experiments on water, but in this case the operation included the titration of the dilute acid or ammonia in the absorption flasks.

It was necessary to find what pressure was required to drive the air through the whole apparatus without neutralising any of the acid. This was effected by ascertaining the pressures necessary to drive the air (1) through the ammonia solution alone, and (2) through the acid solution and the rest of the apparatus; the sum of the two pressures was the amount required, and the gauge (*Proc. Roy. Soc., ibid.*, Fig. 1) was adjusted to this pressure before beginning the experiment.

The strength of the ammonia solution in the last flask did not usually change appreciably during the experiment, the maximum alteration being only about 1 per cent., but in every experiment the strength was found before and after aspiration, and the mean taken of the two determinations. From 2 to 10 c.c. were withdrawn by carefully standardised pipettes, run into an excess of standard acid, and titrated with standard caustic soda solution, the temperature being maintained at 15°. The percentage strength was calculated from Lunge and Wiernik's data (Landolt and Börnstein's *Tabellen*, 221). The neutralisation of the acid in the absorption flask was shown by some methyl orange present, and the aspiration was not allowed to continue long after this point was reached. Acid solutions of various strengths had to be used to suit the varying concentration of the ammonia solution and the different amounts of ammonia solution withdrawn; these were standardised by means of sodium carbonate, and also with ammonium chloride and a caustic soda solution.

A series of experiments was always begun with a strong solution, and the remaining solution was diluted down for the succeeding experiment. The ammonia solution employed was obtained by distilling the pure concentrated solution with barium hydroxide, and passing the gas evolved through barium hydroxide solution and into distilled water; in this way, it was obtained so free from carbon dioxide that it gave, in the worst cases, only a very slight turbidity with barium chloride. A trace of some of the amines was probably present, but this has

been shown not to affect appreciably the vapour pressure of the solution (Trans., 1901, 79, 721).

Experiments were made at every  $10^\circ$  from  $0^\circ$  to  $60^\circ$ . Unfortunately, the method is not applicable over a very wide range of temperature or with very varying concentrations of the solution, for when the vapour pressure becomes nearly equal to the atmospheric pressure, a very little air will draw off a very large quantity of vapour, and, moreover, the evaporation of the ammonia becomes so rapid that it is impossible to keep the temperature constant.

*Calculation of Results.*—The measurements already described, together with that of the barometric height, afford the following data :

$w_a$  = weight of ammonia withdrawn.

$w_w$  = „ water vapour „ (by difference).

$P$  = pressure in last aspiration flask.

$p$  = pressure of air in aspirator (corrected for the vapour pressure of water).

$T$  = absolute temperature of aspirator.

$V$  = volume of water drawn from aspirator.

Assuming the truth of Dalton's law of partial pressures, the following relationship holds good :

$$\frac{\text{pressure of ammonia}}{\text{total pressure}} = \frac{\text{volume of ammonia}}{\text{total volume}},$$

which works out to the following expression (putting  $p_a$  and  $p_w$  = partial pressures of ammonia and water vapour respectively) :

$$p_a = \frac{w_a \times 1.312 \times 760 \times P \times T}{T \times 760(w_a \times 1.312 + w_w \times 1.242) + 273 \times V \times p'}$$

and similarly for the water vapour :

$$p_w = \frac{w_w \times 1.242 \times 760 \times P \times T}{T \times 760(w_w \times 1.242 + w_a \times 1.312) + 273 \times V \times p'}$$

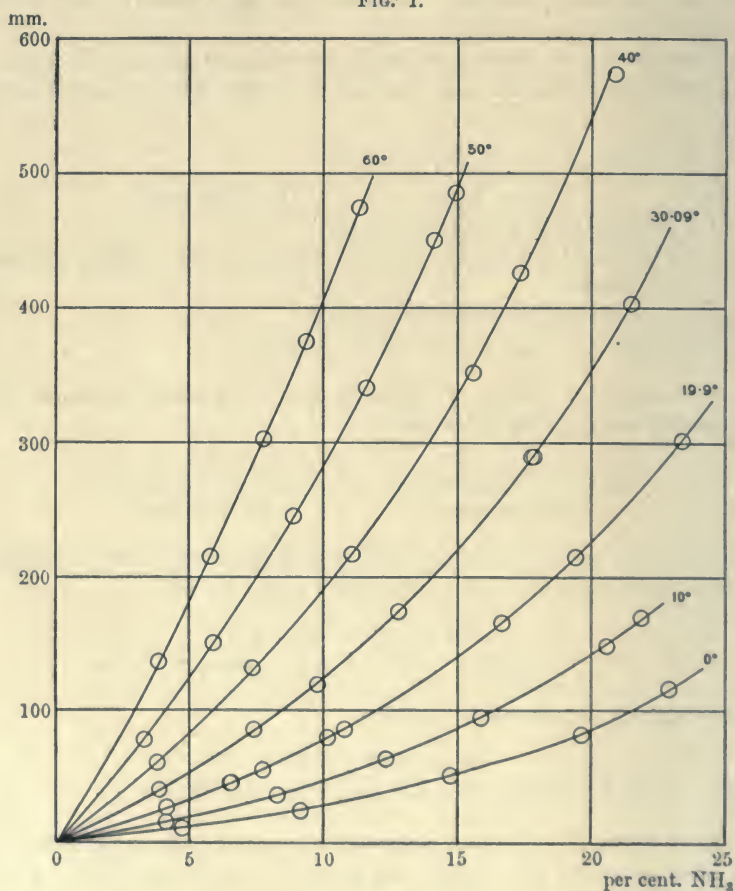
At  $0^\circ$  and under 760 mm. pressure, the specific volume of ammonia is assumed to be 1.312, whilst that of water vapour is taken as 1.242. These values are calculated from the density of oxygen and the molecular weights of the gases. I have shown that this assumption of normal density is justifiable in the case of water vapour (*Proc. Roy. Soc.*, 1903, 72, 80), but there is some doubt as to whether this is the case with ammonia.\* Le Duc found that the density of ammonia at  $0^\circ$  and

\* The value given is 0.5971 (air = 1) (*Compt. rend.*, 1897, 125, 573). This gives the specific volume as 1.295 instead of 1.312, the number employed above.



760 mm. was more than 1 per cent. above the normal value, but when mixed with large quantities of air and water vapour, the density will probably be more nearly normal, assuming that no chemical action takes place. In the absence of exact data on this point, it was thought best to calculate the results on the assumption that the density was normal throughout, especially as the deviation

FIG. 1.



from normal value can hardly be more than the probable experimental error of these results.

*Results obtained.*—The actual experimental results are shown in the table on p. 1173.

From these results, a series of isothermal curves was plotted, Fig. 1 for ammonia, and Fig. 2 (p. 1176) for water vapour, and from them the

| Temperature. | Percentage of ammonia. | Partial pressure of ammonia ( $p_a$ ). | Partial pressure of water vapour ( $p_w$ ). |
|--------------|------------------------|--|---|
| -0°          | 4.72                   | 11.4 mm.                               | 5.1 mm.                                     |
|              | 9.15                   | 24.8 "                                 | 5.3 "                                       |
|              | 14.73                  | 51.3 "                                 | 4.1 "                                       |
|              | 19.62                  | 82.5 "                                 | 3.0 "                                       |
|              | 22.90                  | 116.6 "                                | 2.8 "                                       |
| 10°          | 4.16                   | 16.5 "                                 | 9.1 "                                       |
|              | 8.26                   | 37.2 "                                 | 8.8 "                                       |
|              | 12.32                  | 64.2 "                                 | 7.6 "                                       |
|              | 15.88                  | 95.1 "                                 | 7.0 "                                       |
|              | 20.54                  | 149.2 "                                | 7.2 "                                       |
|              | 21.83                  | 169.8 "                                | 5.5 "                                       |
| 19.9°        | 4.18                   | 27.4 "                                 | 16.4 "                                      |
|              | 6.50                   | 45.8 "                                 | 16.1 "                                      |
|              | 6.55                   | 46.0 "                                 | 16.0 "                                      |
|              | 7.72                   | 56.2 "                                 | 15.6 "                                      |
|              | 10.15                  | 80.6 "                                 | 15.1 "                                      |
|              | 10.75                  | 86.3 "                                 | 14.7 "                                      |
|              | 16.64                  | 166.1 "                                | 12.9 "                                      |
|              | 19.40                  | 215.6 "                                | 12.3 "                                      |
|              | 23.37                  | 302.4 "                                | 10.3 "                                      |
| 30.09°       | 3.93                   | 41.2 "                                 | 31.1 "                                      |
|              | 7.43                   | 86.3 "                                 | 29.2 "                                      |
|              | 9.75                   | 120.0 "                                | 28.5 "                                      |
|              | 12.77                  | 175.0 "                                | 26.6 "                                      |
|              | 17.76                  | 290.2 "                                | 24.8 "                                      |
|              | 17.84                  | 291.1 "                                | 24.3 "                                      |
|              | 21.47                  | 404.6 "                                | 22.1 "                                      |
| 40°          | 3.79                   | 61.1 "                                 | 53.5 "                                      |
|              | 7.36                   | 133.0 "                                | 50.7 "                                      |
|              | 11.06                  | 218.5 "                                | 49.1 "                                      |
|              | 15.55                  | 353.6 "                                | 44.1 "                                      |
|              | 17.33                  | 427.7 "                                | —   |
|              | 20.85                  | 576.1 "                                | 37.8 "                                      |
| 50°          | 3.29                   | 79.1 "                                 | 89.6 "                                      |
|              | 5.90                   | 151.3 "                                | 87.1 "                                      |
|              | 8.91                   | 246.6 "                                | 83.0 "                                      |
|              | 11.57                  | 341.7 "                                | 80.6 "                                      |
|              | 14.15                  | 451.4 "                                | 77.0 "                                      |
|              | 14.94                  | 487.1 "                                | 75.2 "                                      |
| 60°          | 3.86                   | 136.9 "                                | 144.1 "                                     |
|              | 5.77                   | 215.9 "                                | —   |
|              | 7.78                   | 300.4 "                                | 138.5 "                                     |
|              | 9.37                   | 375.7 "                                | 135.5 "                                     |
|              | 11.31                  | 475.8 "                                | 130.4 "                                     |

pressures were read for concentrations of 2·5, 5·0, &c., per cent. of ammonia. The "isosthens" were then constructed from the numbers obtained; but it has not been thought necessary to reproduce them. These curves, which were drawn directly without smoothing through the points from the isothermals, may be regarded as being straight lines over intervals of 2°, and the values have been read off and tabulated, both for ammonia and water vapour. The following table furnishes the isothermals when read horizontally and the isosthens when read vertically; intermediate values may be found with fair accuracy by taking proportional parts.

*Percentage of Ammonia.*

| Temp. | 2·5  | 5·0   | 7·5   | 10·0  | 12·5  | 15·0  | 17·5  | 20·0  | 22·5  |
|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0°    | 6    | 13    | 20    | 28·5  | 40    | 53·5  | 69    | 87·5  | 111   |
| 2     | 6·5  | 14·5  | 22    | 31·5  | 43·5  | 58·5  | 76    | 97    | 123   |
| 4     | 7    | 15    | 24    | 34·5  | 48    | 64·5  | 83·5  | 107   | 135·5 |
| 6     | 7·5  | 16·5  | 26·5  | 38    | 53    | 71    | 92    | 118   | 149   |
| 8     | 8    | 18    | 29·5  | 42·5  | 58·5  | 78    | 102   | 130   | 163·5 |
| 10    | 9    | 20    | 32·5  | 47·5  | 65    | 86·5  | 112   | 143   | 179·5 |
| 12    | 10   | 22    | 36    | 52    | 71·5  | 95·5  | 123·5 | 157·5 | 196·5 |
| 14    | 11   | 24·5  | 40    | 58    | 79    | 105   | 136   | 173   | 215·5 |
| 16    | 12·5 | 27    | 44·5  | 64    | 87·5  | 115·5 | 150   | 190   | 236   |
| 18    | 14   | 30    | 49    | 71    | 97    | 127·5 | 165   | 208·5 | 258·5 |
| 20    | 15·5 | 33·5  | 54    | 78·5  | 107   | 141   | 181   | 228·5 | 283   |
| 22    | 17   | 37    | 59·5  | 86·5  | 117   | 155   | 198   | 250   | 309   |
| 24    | 18·5 | 40·5  | 65·5  | 95    | 128   | 170   | 217   | 273   | 337   |
| 26    | 20·5 | 44·5  | 72    | 104   | 141   | 186   | 236·5 | 298   | 368   |
| 28    | 22·5 | 49    | 78·5  | 114   | 154·5 | 202·5 | 258   | 324·5 | 403   |
| 30    | 25   | 54    | 86    | 124·5 | 169   | 220   | 281   | 353   | 441·5 |
| 32    | 27·5 | 58·5  | 94    | 136   | 184·5 | 241   | 306   | 382·5 | —     |
| 34    | 30   | 64    | 103   | 149   | 201   | 263   | 334   | 415   | —     |
| 36    | 32·5 | 70    | 112·5 | 162   | 219   | 286·5 | 363   | 451   | —     |
| 38    | 35   | 76·5  | 122·5 | 176   | 238   | 311   | 395   | 491   | —     |
| 40    | 38   | 83·5  | 134   | 191   | 258·5 | 336   | 429   | 535   | —     |
| 42    | 42   | 91    | 145·5 | 208   | 280   | 363·5 | 466   | —     | —     |
| 44    | 46   | 99    | 158   | 225·5 | 302·5 | 392·5 | —     | —     | —     |
| 46    | 50   | 107·5 | 172   | 244   | 327   | 422·5 | —     | —     | —     |
| 48    | 54·5 | 116·5 | 186   | 263   | 352   | 455·5 | —     | —     | —     |
| 50    | 59   | 126   | 200·5 | 284·5 | 380   | 491·5 | —     | —     | —     |
| 52    | 64   | 136   | 217   | 306   | —     | —     | —     | —     | —     |
| 54    | 69·5 | 147   | 233·5 | 329   | —     | —     | —     | —     | —     |
| 56    | 75   | 158·5 | 251   | 354   | —     | —     | —     | —     | —     |
| 58    | 80   | 170·5 | 270   | 380   | —     | —     | —     | —     | —     |
| 60    | 85·5 | 183   | 291   | 406·5 | —     | —     | —     | —     | —     |



## Percentage of Ammonia.

| Temp.                                   | 0     | 2.5   | 5.0  | 7.5   | 10.0  | 12.5  | 15.0 | 17.5 | 20.0 | 22.5 |
|---|-------|-------|------|-------|-------|-------|------|------|------|------|
| Partial pressure of water vapour in mm. |       |       |      |       |       |       |      |      |      |      |
| 0°                                      | 4.5   | 4.5   | 4    | 4     | 4     | 3.5   | 3.5  | 3.5  | 3    | 3    |
| 2                                       | 5.5   | 5     | 5    | 5     | 4.5   | 4     | 4    | 4    | 3.5  | 3.5  |
| 4                                       | 6     | 6     | 6    | 5.5   | 5     | 4.5   | 4.5  | 4.5  | 4    | 4    |
| 6                                       | 7     | 7     | 7    | 6.5   | 6     | 5.5   | 5.5  | 5.5  | 4.5  | 4.5  |
| 8                                       | 8     | 8     | 8    | 7.5   | 7     | 6.5   | 6.5  | 6.5  | 5.5  | 5    |
| 10                                      | 9     | 9     | 9    | 8.5   | 8     | 7.5   | 7.5  | 7.5  | 6.5  | 6    |
| 12                                      | 10.5  | 10.5  | 10   | 9.5   | 9     | 8.5   | 8.5  | 8.5  | 7.5  | 7    |
| 14                                      | 12    | 12    | 11.5 | 11    | 10.5  | 10    | 9.5  | 9.5  | 8.5  | 8    |
| 16                                      | 13.5  | 13.5  | 13   | 12    | 12    | 11.5  | 11   | 11   | 10   | 9    |
| 18                                      | 15.5  | 15    | 14.5 | 14    | 13.5  | 13    | 12.5 | 12.5 | 11.5 | 10   |
| 20                                      | 17.5  | 17    | 16.5 | 15.5  | 15    | 14.5  | 14   | 14   | 13   | 11.5 |
| 22                                      | 20    | 19    | 18.5 | 17.5  | 17    | 16.5  | 16   | 16   | 14.5 | 13   |
| 24                                      | 22.5  | 21.5  | 21   | 20    | 19.5  | 18.5  | 18   | 18   | 16.5 | 14.5 |
| 26                                      | 25    | 24    | 23.5 | 22    | 21.5  | 21    | 20.5 | 20   | 18.5 | 16.5 |
| 28                                      | 28.5  | 27    | 26.5 | 25    | 24.5  | 23.5  | 23   | 22   | 20.5 | 18.5 |
| 30                                      | 31.5  | 30.5  | 30   | 28.5  | 28    | 26.5  | 25.5 | 24.5 | 23   | 20.5 |
| 32                                      | 35.5  | 34.5  | 34   | 32.5  | 31.5  | 30    | 28.5 | 27.5 | 26   | 23   |
| 34                                      | 40    | 38.5  | 38   | 36.5  | 35.5  | 33.5  | 32   | 31   | 29   | 26   |
| 36                                      | 44.5  | 43    | 42.5 | 41    | 39.5  | 37.5  | 36   | 34.5 | 32   | 29   |
| 38                                      | 49.5  | 48    | 47.5 | 46    | 44.5  | 42.5  | 40.5 | 38   | 35.5 | 32   |
| 40                                      | 55    | 54    | 53   | 51.5  | 49.5  | 47.5  | 45   | 42.5 | 39.5 | 36   |
| 42                                      | 61.5  | 60    | 58.5 | 57    | 55    | 53    | 50.5 | 47   | 43.5 | —    |
| 44                                      | 68    | 66.5  | 65   | 63.5  | 61.5  | 59    | 56   | —    | —    | —    |
| 46                                      | 75.5  | 73.5  | 71.5 | 70    | 68    | 65    | 62   | —    | —    | —    |
| 48                                      | 83.5  | 81.5  | 79   | 77.5  | 75.5  | 72    | 68.5 | —    | —    | —    |
| 50                                      | 92.5  | 90    | 87.5 | 85.5  | 82.5  | 79.5  | 75.5 | —    | —    | —    |
| 52                                      | 102   | 99    | 96.5 | 94    | 91    | 87.5  | 83   | —    | —    | —    |
| 54                                      | 112.5 | 109   | 107  | 103.5 | 100.5 | 96    | —    | —    | —    | —    |
| 56                                      | 123.5 | 120   | 118  | 114.5 | 111   | 106   | —    | —    | —    | —    |
| 58                                      | 136   | 132.5 | 130  | 126.5 | 122   | 117   | —    | —    | —    | —    |
| 60                                      | 149.5 | 146.5 | 143  | 139   | 134   | 128.5 | —    | —    | —    | —    |

*Relation between the Partial Pressures and Concentration.*—As I pointed out in a former paper (Trans., 1901, 79, 724), an aqueous solution of ammonia may be regarded as a mixture of two liquids, the boiling points of which are far removed from each other, and the vapour pressures should therefore follow the laws of vapour pressure of mixed liquids as worked out by Duhem, Margules, and others. Excellent accounts of the subject are given by Zawidski (*Zeit. physikal. Chem.*, 1900, 35, 157) and by Ostwald in his *Lehrbuch der allgemeinen Chemie* (2nd edition, vol. ii, p. 636). The relation between the partial pressures and the concentration of the solution, deduced from thermodynamical considerations, is

$$\frac{d \log p_1}{d \log x} = \frac{d \log p_2}{d \log (1-x)},$$

or

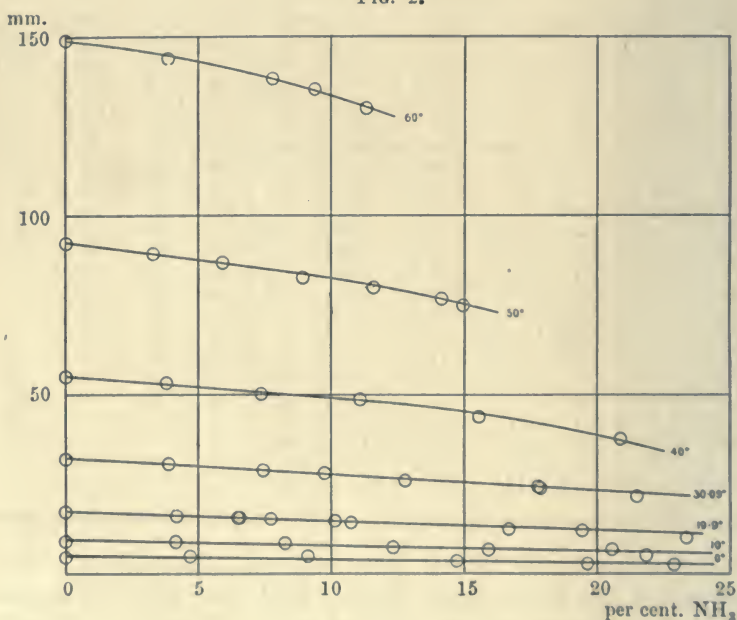
$$\frac{dp_1}{dp_2} = -\frac{p_1}{p_2} \cdot \frac{1-x}{x},$$

where

$p_1$  = partial pressure of one constituent (say ammonia),  
 $p_2$  = " " " the other " (water),  
 $x$  =  $\frac{\text{no. of molecules of ammonia in the liquid mixture.}}{\text{Total no. of molecules.}}$

This equation can only be integrated by making certain arbitrary assumptions as to the relation between the partial pressure of one

FIG. 2.



constituent and the vapour pressure of the pure liquid. It has been thought best, therefore, to test the differential equation as it stands. The values of  $dp_1$  have been obtained from the table already given, the average of two differences, each over a variation of concentration of 2.5 per cent., being taken.

Values of  $dp_2$  are very difficult to obtain with any accuracy owing to their small magnitude.

The curves at 0° and 10° are straight, and therefore  $dp_2$  has a uniform value, which has been calculated directly from the first and last readings of  $p_2$ .

At the higher temperatures, the values have been found by drawing tangents by eye; this method is capable of considerable accuracy, as was shown in a previous paper (Trans., 1901, 79, 723). The results are now tabulated:

| Temp. | $x$    | $1-x$  | $p_1$ | $p_2$ | $dp_1$ | $dp_2$ | $-\frac{p_1(1-x)}{p_2 x}$ | $\frac{dp_1}{dp_2}$ |
|-------|--------|--------|-------|-------|--------|--------|---------------------------|---------------------|
| 0°    | 0.0527 | 0.9473 | 13    | 4.0   | 7      | 0.19   | 58.4                      | 36.8                |
|       | 0.1050 | 0.8950 | 28.5  | 4.0   | 10     | 0.19   | 60.7                      | 52.0                |
|       | 0.1571 | 0.8429 | 53.5  | 3.5   | 14.5   | 0.19   | 82.0                      | 76.3                |
|       | 0.2088 | 0.7912 | 87.5  | 3.0   | 21     | 0.19   | 110.5                     | 110.5               |
| 10°   | 0.0527 | 0.9473 | 20    | 9     | 11.75  | 0.375  | 39.9                      | 31.3                |
|       | 0.1050 | 0.8950 | 47.5  | 8     | 16.2   | 0.375  | 50.6                      | 43.2                |
|       | 0.1571 | 0.8429 | 86.5  | 7.5   | 23.5   | 0.375  | 61.9                      | 62.7                |
|       | 0.2088 | 0.7912 | 143   | 6.5   | 33.75  | 0.375  | 83.4                      | 90.0                |
| 20°   | 0.0527 | 0.9473 | 33.5  | 16.5  | 19.25  | 0.60   | 36.5                      | 32.1                |
|       | 0.1050 | 0.8950 | 78.5  | 15    | 26.5   | 0.60   | 44.6                      | 44.2                |
|       | 0.1571 | 0.8429 | 141   | 14    | 37     | 0.825  | 54.0                      | 44.9                |
|       | 0.2088 | 0.7912 | 228.5 | 13    | 51     | 0.825  | 66.6                      | 61.8                |
| 30°   | 0.0527 | 0.9473 | 54    | 30    | 30.5   | 0.975  | 32.4                      | 31.3                |
|       | 0.1050 | 0.8950 | 124.5 | 28    | 41.5   | 1.1    | 37.9                      | 37.7                |
|       | 0.1571 | 0.8429 | 220   | 25.5  | 56.0   | 1.2    | 46.3                      | 46.7                |
|       | 0.2088 | 0.7912 | 353   | 23    | 80.2   | 1.3    | 58.2                      | 61.7                |
| 40°   | 0.0527 | 0.9473 | 83.5  | 53    | 48.0   | 1.34   | 28.3                      | 35.8                |
|       | 0.1050 | 0.8950 | 191   | 49.5  | 62.2   | 1.85   | 32.9                      | 33.6                |
|       | 0.1571 | 0.8429 | 336   | 45    | 85.2   | 2.44   | 40.1                      | 34.9                |
| 50°   | 0.0527 | 0.9473 | 126   | 87.5  | 70.7   | 2.32   | 25.7                      | 30.5                |
|       | 0.1050 | 0.8950 | 234.5 | 82.5  | 89.7   | 2.98   | 29.4                      | 30.1                |
| 60°   | 0.0527 | 0.9473 | 183   | 143   | 102.7  | 3.76   | 23.0                      | 27.3                |

The agreement between the values of  $\frac{dp_1}{dp_2}$  and  $-\frac{p_1}{p_2} \cdot \frac{1-x}{x}$  is as close as can be expected, considering the very large errors which may arise in determining  $dp_2$ , and the differences are evenly distributed.

The partial pressure of the ammonia does not follow Henry's law, as can be seen at once from the curvature of the isothermals. The curves for water are, however, straight, or very nearly straight, over a considerable range of concentration, that is to say, the partial pressure of the water vapour is proportional to  $1-x$  (law of Raoult and van't Hoff),  $p_2 = P_2(1-x)$ , where  $P_2$  = vapour pressure of pure water. The agreement is found to be very good up to a 10 per cent. ammonia solution:



| Temperature. | $P_2$ . | $(1-x)$ . | $P_2(1-x)$ . | $p_2$ . |
|--------------|---------|-----------|--------------|---------|
| 0°           | 4.6     | 0.947 *   | 4.3          | 4.0     |
|              |         | 0.895     | 4.1          | 4.0     |
|              |         | 0.843     | 3.9          | 3.5     |
|              |         | 0.791     | 3.6          | 3.0     |
| 10°          | 9.2     | 0.947     | 8.7          | 9.0     |
|              |         | 0.895     | 8.2          | 8.0     |
|              |         | 0.843     | 7.8          | 7.5     |
|              |         | 0.791     | 7.3          | 6.5     |
| 20°          | 17.5    | 0.947     | 16.6         | 16.5    |
|              |         | 0.895     | 15.7         | 15.0    |
|              |         | 0.843     | 14.8         | 14.0    |
|              |         | 0.791     | 13.8         | 13.0    |
| 30°          | 31.7    | 0.947     | 30.0         | 30.0    |
|              |         | 0.895     | 28.4         | 28.0    |
|              |         | 0.843     | 26.7         | 25.5    |
|              |         | 0.791     | 25.1         | 23.0    |
| 40°          | 55.2    | 0.947     | 52.3         | 53.0    |
|              |         | 0.895     | 49.4         | 49.5    |
|              |         | 0.843     | 46.5         | 45.0    |
|              |         | 0.791     | 43.7         | 39.5    |
| 50°          | 92.3    | 0.947     | 87.5         | 87.5    |
|              |         | 0.895     | 82.7         | 82.5    |
|              |         | 0.843     | 77.8         | 75.5    |
| 60°          | 149.3   | 0.947     | 141.4        | 143.0   |
|              |         | 0.895     | 133.6        | 134.0   |

\* These values of  $1-x$  correspond with 5, 10, 15, and 20 per cent. of ammonia respectively.

This close agreement shows that the molecular weight of ammonia in solution is normal, and that there cannot be a large amount of any hydrate formed.

#### *Relation between Partial Pressure and Temperature.*

The relation appears to be simplest at the highest concentrations; with 22.5 per cent. ammonia solution, the expression  $\log p = a + bt$  holds good to within 1 per cent. With a concentration of 20 per cent., another term must be introduced, whilst at lower concentrations still more terms would be necessary.

(20 per cent.)  $\log p = a + bt + ct^2$ ,  $a = 1.942$ ,  $b = 0.02195$ ,  
 $c = -0.0000575$ .

| Temperature. | <i>p</i> (found). | <i>p</i> (calculated). |
|--------------|-------------------|------------------------|
| 0°           | 87·5              | (87·5)                 |
| 10           | 143               | 143                    |
| 20           | 228·5             | 228                    |
| 30           | 353               | 354                    |
| 40           | 535               | 535                    |

(22.5 per cent.)  $\log p = a + bt$ ,  $a = 2.051$ ,  $b = 0.0199$ .

| Temperature. | $p$ (found). | $p$ (calculated). |
|--------------|--------------|-------------------|
| 0°           | 111          | 112               |
| 6            | 149          | 148               |
| 12           | 196·5        | 195               |
| 18           | 258·5        | 256·5             |
| 24           | 337          | 338               |
| 30           | 441·5        | 445               |

As the formula is purely empirical, it has not been extended to suit the lower concentrations.

No simple formula has been found to represent the relationship between temperature and the partial pressure of the water vapour.

*Comparison of the Total Vapour Pressures obtained by the Two Methods.*

In the following table are given the vapour pressures measured by the statical method (static), and the sums of the partial pressures of the ammonia and the water vapour (air-current):—

[illegible]

| Percentage<br>of<br>ammonia. | 20°.    |                  | 10°.    |                  | 0°.     |                  |
|------------------------------|---------|------------------|---------|------------------|---------|------------------|
|                              | Static. | Air-<br>current. | Static. | Air-<br>current. | Static. | Air-<br>current. |
| 2.5                          | 32.5    | 32               | 18      | 18               | 13      | 10.4             |
| 5.0                          | 47.5    | 50               | 27      | 29               | 20      | 17               |
| 7.5                          | 70      | 70               | 40      | 41               | 27.5    | 24               |
| 10.0                         | 93      | 94               | 54      | 56               | 35      | 32               |
| 12.5                         | 118     | 122              | 69      | 73               | 45      | 43.5             |
| 15.0                         | 151     | 155              | 89      | 94               | 57      | 57               |
| 17.5                         | 190     | 194              | 115     | 119.5            | 75      | 72               |
| 20.0                         | 237     | 241              | 144     | 150              | 93      | 90.5             |
| 22.5                         | 291     | 294              | 180.5   | 186              | 117     | 114              |

At the higher temperatures, the agreement is seen to be fairly close, and as a rule within 1 per cent. At the lower temperatures, the experimental error is much larger in both methods; in the statical method, a trace of air would produce a considerable error, whilst in the air-current method, the amounts of ammonia and water vapour aspirated off are comparatively small. On the whole, there is a tendency for the results by the air-current method to be somewhat higher than the others, and I believe this to be due to the abnormal density of ammonia gas. For want of exact information on the matter, the density has been taken as normal in calculating out the vapour pressures. If the density had been taken as being somewhat smaller, and the specific volume therefore as greater, the agreement would have been closer. It follows from these results that the sum of the partial pressures is equal to the total pressure, and there is no large deviation from Dalton's law in the case of mixtures of air, ammonia, and aqueous vapour; consequently there cannot be any appreciable quantity of a hydrate of ammonia present in the vapour drawn off from the solution.

*Relation between Partial Pressure and "Rate of Escape."*

In a former paper (Trans., 1898, 73, 515), it was shown that if a current of air is aspirated through a single flask of ammonia solution, the quantity of ammonia in solution  $q$ , after the passage of  $V$  litres of air, can be accurately represented by the equation  $\log q = a - bV$ ,  $a$  and  $b$  being constants ( $a$  is the logarithm of the amount in solution at the beginning of the experiment). By differentiating the equation, we obtain  $\frac{dq}{dV} = bq$ ;  $b$  represents, therefore, the amount of ammonia that would be drawn off by one litre of air, supposing the solution to con-



tain always one gram of ammonia, and is therefore a measure of the "rate of escape" of the ammonia.

In order to deduce the partial pressure of the ammonia from the rate of escape, it is necessary to find a mean concentration of the solution so that a solution of this strength would give up to the air as much ammonia as was given up by the actual solution of varying concentration.

Let  $c$  = the real mean concentration (grams of ammonia in 50 c.c. of the solution).

$V$  = vol. of air (litres) passed through the solution measured as dry air at the temperature and pressure of the solution.

$w_a$  = amount of ammonia drawn off (grams).

Thus  $w_a = \frac{bcV}{0.4343}$ , correcting for the reduction from natural logarithms to logarithms to base 10, and  $c = \frac{0.4343w_a}{bV}$ .

Let  $P$  = the total pressure.

$p_a$  = partial pressure of the ammonia.

$p_w$  = " " water vapour.

$v_a$  = volume of the ammonia drawn off.

$s_a$  = specific volume of the ammonia at the temperature and pressure of the solution.

Then from Dalton's law :

$$\begin{aligned} \frac{P - p_w}{p_a} &= \frac{V + v_a}{v_a} = 1 + \frac{V}{v_a} = 1 + \frac{V}{w_a s_a} \\ &= 1 + \frac{V}{cVb s_a} = 1 + \frac{0.4343}{cb s_a} \\ \therefore p_a &= \frac{P - p_w}{1 + \frac{0.4343}{cb s_a}} \end{aligned}$$

Several cases have been tested, in which all the data are derived from the paper on the "rate of escape" except the values of  $p_w$ , which are taken from the present communication.

20°.  $P = 766$ ,  $p_w = 16$ ,  $s_a = 1.397$ ,  $b = 0.00655$ ,  $c = 2.880$  (5.90 per cent.  $\text{NH}_3$ ).

$p_a = 42.9$ . Read from isothermal 41.2.

30°.  $P = 758$ ,  $p_w = 30$ ,  $s_a = 1.460$ ,  $b = 0.01034$ ,  $c = 2.869$  (5.88 per cent.  $\text{NH}_3$ ).

$p_a = 66.0$ . Read from isothermal 65.0.

40°.  $P = 765$ ,  $p_w = 53$ ,  $s_a = 1.494$ ,  $b = 0.0165$ ,  $c = 2.449$  (5.00 per cent.  $\text{NH}_3$ ).

$p_a = 86.9$ . Read from isothermal 84.0.

The agreement is not good, and there appears to be some constant error. The present experiments are far more accurate than the older ones, and the latter are probably not of much use for giving absolute values of the partial pressure.

*Latent Heat of Evaporation of Aqueous Ammonia Solution.*

The latent heat of evaporation of solutions of various concentrations has been calculated from the thermodynamical equation  $L = \frac{T'}{J}(s' - s)\frac{dp}{dT}$ . The specific volume of the mixed vapour,  $s'$ , has been taken as the sum of the specific volumes of the ammonia and water vapour present;  $s$  has been neglected. Values of  $\frac{dp}{dT}$  have been calculated from the table of total pressures, and also from the partial pressures (by taking the sum of the two differences); the mean of the two results has been used in the calculations.

| Percent-<br>age of<br>ammonia. | $\frac{dp}{dT}$ at 13°.    |                               | Mean. | $S'$ . | $L$ . | $L'$ . | $\Delta L$ . |
|--------------------------------|----------------------------|-------------------------------|-------|--------|-------|--------|--------------|
|                                | From<br>total<br>pressure. | From<br>partial<br>pressures. |       |        |       |        |              |
| 10.0                           | 3.5                        | 3.75                          | 3.625 | 15.66  | 516.3 | 560    | 44           |
| 12.5                           | 4.25                       | 4.5                           | 4.375 | 12.27  | 488.3 | 552    | 64           |
| 15.0                           | 5.75                       | 5.25                          | 5.5   | 9.53   | 476.7 | 545    | 68           |
| 17.5                           | 6.75                       | 6.75                          | 6.75  | 7.47   | 458.6 | 537    | 78           |
| 20.0                           | 8.5                        | 8.25                          | 8.375 | 5.97   | 454.8 | 530    | 75           |
| 22.5                           | 10.0                       | 10.0                          | 10.0  | 4.792  | 435.9 | 523    | 87           |
| 25.0                           | 12.25                      | —                             | —     | 3.847  | 428.7 | 515    | 86           |
| 27.5                           | 14.75                      | —                             | —     | 3.132  | 420.2 | 508    | 88           |
| 30.0                           | 17.25                      | —                             | —     | 2.548  | 399.8 | 501    | 101          |

The column headed  $L'$  contains the values of the heat of evaporation calculated on the assumption that it is simply the sum of the heats of evaporation of the ammonia and the water present in the mixture. The column  $\Delta L$  contains values of  $L' - L$ , which should represent the heat evolved on mixing the ammonia, in the liquid form, with the water.

The heat of solution of ammonia is given by Thomsen (*Thermochemische Untersuchungen*, vol. 2, p. 68) as  $\text{NH}_3, \text{Aq} = 8430$ ; this gives the heat of solution per gram of ammonia as 496, and subtracting from this the heat of evaporation of ammonia, 295, we get 201 as the

heat evolved on mixing 1 gram of liquid ammonia with a large quantity of water. The value  $L=295$  is obtained from Regnault's results, taking the mean of the values of  $L$  and the mean of the temperatures (Landolt and Börnstein's *Tabellen*).

The above values of  $\Delta L$  are vitiated by the large error inherent in the ratio  $\frac{dp}{dT}$  from which  $L$  is calculated, but, nevertheless, they are of the order which would be expected from the numerical data just given.

### *Summary and General Conclusions.*

(1) The partial vapour pressures of aqueous ammonia solution have been found and tabulated for concentrations up to 22.5 per cent. ammonia, and at temperatures from 0 to 60°.

(2) The relationship between the partial pressures and the concentration of the solution is found to be that deduced by Duhem and others for binary mixtures of liquids.

(3) The lowering of the vapour pressure of water by the ammonia follows Raoult's law closely, showing that the molecular weight of ammonia in solution is normal, and that no large quantity of a hydrate is formed.

(4) The relation between the partial pressure of the ammonia and temperature is expressed by a formula of the form,  $\log p = a + bt + \dots$

(5) The sum of the partial pressures is equal to the total pressure found by the statical method; consequently there is no appreciable quantity of hydrate present in the gaseous mixture given off by the solution.

(6) The relationship between the partial pressure of the ammonia and the "rate of escape" has been deduced.

(7) The approximate latent heats of evaporation of aqueous ammonia-solution of various concentrations have been calculated.

The experimental part of this work was carried out at the Physik-  
alisch-chemisches Institut, Leipzig, and I am much indebted to the director, Prof. Ostwald, and the sub-director, Dr. Luther, for the facilities they so readily afforded me.

The expense incurred for apparatus was covered by a grant from the Research Fund of the Chemical Society.



*Appendix.—Experimental Data.*

| Temperature of solution. | Percentage of ammonia. | $W_a$<br>grams. | $W_w$<br>grams. | $P$<br>mm. | $V$<br>litres. | $T$<br>ab-<br>solute. | $p$<br>mm. | Partial pressures. |       |
|--------------------------|------------------------|-----------------|-----------------|------------|----------------|-----------------------|------------|--------------------|-------|
|                          |                        |                 |                 |            |                |                       |            | $p_a$<br>mm.       | $p_w$ |
| 0°                       | 19.62                  | 0.8274          | 0.0321          | 734.7      | 10             | 296.0                 | 703.7      | 82.5               | 3.0   |
|                          | 14.73                  | 0.4992          | 0.0416          | 737.9      | 10             | 293.7                 | 712.1      | 51.3               | 4.1   |
|                          | 9.15                   | 0.2350          | 0.0527          | 745.2      | 10             | 292.2                 | 723.5      | 24.8               | 5.3   |
|                          | 4.72                   | 0.1058          | 0.0500          | 742.5      | 10             | 292.0                 | 719.5      | 11.4               | 5.1   |
|                          | 22.90                  | 1.257           | 0.0320          | 739.4      | 10             | 292.6                 | 713.8      | 116.6              | 2.8   |
| 10°                      | 8.26                   | 0.3588          | 0.0892          | 734.7      | 10             | 292.5                 | 709.8      | 37.2               | 8.8   |
|                          | 4.16                   | 0.1547          | 0.0898          | 726.8      | 10             | 292.4                 | 702.2      | 16.5               | 9.1   |
|                          | 20.54                  | 1.385           | 0.0710          | 741.5      | 8.084          | 291.8                 | 716.2      | 149.2              | 7.2   |
|                          | 12.32                  | 0.6452          | 0.0803          | 731.5      | 10             | 291.8                 | 706.2      | 64.2               | 7.6   |
|                          | 21.83                  | 2.010           | 0.0690          | 735.4      | 10             | 293.4                 | 710.7      | 169.3              | 5.5   |
|                          | 15.88                  | 0.9958          | 0.0777          | 739.0      | 10             | 292.7                 | 713.3      | 95.1               | 7.0   |
| 19.9°                    | 6.50                   | 0.2307          | 0.0858          | 745.5      | 5              | 288.2                 | 724.7      | 45.8               | 16.1  |
|                          | 6.55                   | 0.4593          | 0.1692          | 739.4      | 10             | 290.6                 | 718.3      | 46.0               | 16.0  |
|                          | 4.18                   | 0.2653          | 0.1682          | 739.4      | 10             | 291.8                 | 717.8      | 27.4               | 16.4  |
|                          | 10.75                  | 0.9062          | 0.1636          | 738.7      | 10             | 292.8                 | 715.6      | 86.3               | 14.7  |
|                          | 7.72                   | 0.5594          | 0.1636          | 742.5      | 10             | 294.3                 | 717.0      | 56.2               | 15.6  |
|                          | 23.37                  | 2.918           | 0.1025          | 740.0      | 6              | 294.8                 | 711.6      | 302.4              | 10.3  |
|                          | 16.64                  | 1.977           | 0.1625          | 736.0      | 10             | 293.7                 | 711.2      | 166.1              | 12.9  |
|                          | 10.15                  | 0.8450          | 0.1670          | 730.9      | 10             | 291.0                 | 707.9      | 80.6               | 15.1  |
|                          | 19.40                  | 2.845           | 0.1710          | 738.0      | 10             | 291.0                 | 715.7      | 215.6              | 12.3  |
| 30.09°                   | 17.84                  | 2.328           | 0.2050          | 736.0      | 5              | 290.5                 | 713.6      | 291.1              | 24.3  |
|                          | 7.43                   | 0.4665          | 0.1667          | 734.4      | 5              | 291.0                 | 711.1      | 86.3               | 29.2  |
|                          | 3.93                   | 0.2090          | 0.1663          | 735.1      | 5              | 291.0                 | 713.8      | 41.2               | 31.1  |
|                          | 17.76                  | 2.304           | 0.2080          | 741.7      | 5              | 290.2                 | 713.1      | 290.2              | 24.8  |
|                          | 12.77                  | 1.098           | 0.1765          | 740.7      | 5              | 290.4                 | 717.9      | 175.0              | 26.6  |
|                          | 9.75                   | 0.6843          | 0.1717          | 740.3      | 5              | 290.6                 | 716.3      | 120.0              | 28.5  |
|                          | 21.47                  | 4.397           | 0.2540          | 733.5      | 5              | 291.5                 | 710.0      | 404.6              | 22.1  |
|                          |                        |                 |                 |            |                |                       |            |                    |       |
| 40.00°                   | 15.55                  | 3.445           | 0.4535          | 743.9      | 5              | 292.0                 | 719.1      | 353.6              | 44.1  |
|                          | 11.06                  | 1.541           | 0.3660          | 747.6      | 5              | 292.4                 | 722.9      | 218.5              | 49.1  |
|                          | 7.36                   | 0.7995          | 0.3220          | 747.0      | 5              | 292.4                 | 722.8      | 133.0              | 50.7  |
|                          | 3.79                   | 0.3280          | 0.3035          | 749.4      | 5              | 292.1                 | 726.3      | 61.1               | 53.5  |
|                          | 17.33                  | 5.135           | —               | 750.0      | 5              | 292.4                 | 723.7      | 427.7              | —     |
|                          | 20.85                  | 6.539           | 0.4530          | 746.0      | 2.218          | 292.3                 | 721.6      | 576.1              | 37.8  |
| 50.00°                   | 14.94                  | 4.258           | 0.6945          | 736.1      | 2.305          | 294.0                 | 707.9      | 487.1              | 75.2  |
|                          | 8.91                   | 1.208           | 0.4294          | 735.9      | 3              | 293.2                 | 710.7      | 246.6              | 83.0  |
|                          | 11.57                  | 2.944           | 0.7340          | 730.2      | 4              | 292.2                 | 707.5      | 341.7              | 80.6  |
|                          | 5.90                   | 0.8115          | 0.4937          | 735.9      | 4              | 292.0                 | 711.6      | 151.3              | 87.1  |
|                          | 3.29                   | 0.3766          | 0.4509          | 736.1      | 4.030          | 291.6                 | 713.5      | 79.1               | 89.6  |
|                          | 14.15                  | 1.488           | 0.2610          | 736.9      | 1              | 292.0                 | 713.6      | 451.4              | 77.0  |
|                          |                        |                 |                 |            |                |                       |            |                    |       |
| 60.00°                   | 11.31                  | 2.924           | 0.8470          | 737.9      | 1.217          | 292.8                 | 711.6      | 475.8              | 130.4 |
|                          | 7.78                   | 1.336           | 0.6510          | 740.6      | 2              | 292.6                 | 717.0      | 300.4              | 138.5 |
|                          | 9.37                   | 2.171           | 0.8270          | 742.0      | 2              | 293.8                 | 716.2      | 375.7              | 135.5 |
|                          | 5.77                   | 0.3719          | —               | 741.4      | 1              | 292.8                 | 717.3      | 215.9              | —     |
|                          | 3.86                   | 0.4007          | 0.4455          | 740.6      | 2              | 292.0                 | 717.3      | 136.9              | 144.1 |

CXVI.—*Isomeric Aminoamidines of the Naphthalene Series. (Fourth Communication on Anhydro-bases.)*

By RAPHAEL MELDOLA, F.R.S., JOHN VARGAS EYRE, and JOSEPH HENRY LANE.

IN the last paper dealing with this subject, by one of the authors and Lewis Eynon (Trans., 1900, 77, 1159), it was definitely established that 2:4-dinitro- $\alpha$ -acetonaphthalide gives rise to different aminoamidines according as the reduction is effected by tin and hydrochloric acid (method of Meldola and Streatfeild) or by iron and hydrochloric acid (method of Markfeldt). The isomeric bases are for brevity referred to as Markfeldt's and M. and S. base respectively. The investigation has been extended with the object of ascertaining the cause of this remarkable isomerism. Although the problem cannot yet be considered to be finally solved, a considerable quantity of fresh experimental evidence has enabled us to arrive, at any rate provisionally, at a sufficiently definite conclusion concerning the structural formulæ of the bases. These formulæ will be considered in a subsequent paper after the complete evidence has been submitted. The main facts brought out in the present paper are that the isomerism of the aminoamidines extends to the amidines themselves, and that the M. and S. base is convertible into its isomeride by the prolonged action of iron and hydrochloric acid. Incidentally, many new salts and derivatives of both bases have been prepared and are described in the following pages.

*Ethenyltriaminonaphthalene; the Free Base (M. and S.).*

Although the first attempts to isolate the base were unsuccessful, the experiments were renewed, and we are now enabled to describe a method for obtaining this compound. The sulphate in a pasty condition is heated with a strong solution of ammonium carbonate, taking care to add only sufficient of the latter to just basify the sulphate. The point of neutralisation is indicated by the disappearance of the insoluble sulphate owing to the extreme solubility of the base in water. The hot concentrated solution thus obtained is filtered and allowed to remain for some days, when the base separates out in groups of long, flattened prisms of a brownish colour, which are transparent at first but become opaque in the course of a few days when exposed to the air. Although the base is a perfectly definite compound, it possesses no distinctive characters which can be considered satisfactory from a diagnostic point of view. It is a highly hydrated substance with no

definite melting point, and is capable of forming a number of different compounds with water. On combustion, it leaves a dense residue of carbon, which is so refractory that it burns with the greatest difficulty, even when heated for hours in a current of oxygen. For this reason, the analytical results have been of little value. That the compound is the free base is proved by its giving the phenylazo-compound described in a former paper (Trans., 1899, 75, 1016) and, on acetylation, the acetyl derivative of decomposing point 281—284° (Trans., 1900, 77, 1163).\*

The crystalline base, when allowed to dry in the air at the ordinary temperature, shows the following characters on heating in a capillary glass tube: at 70—75°, the crystals become opaque; at 95—103°, incipient fusion is observed, and up to 210° the substance appears to harden again; at 265°, blackening with decomposition takes place.

The air-dried substance furnished the following result on analysis:

0.1308 gave 12.75 c.c. moist nitrogen at 15.4° and 768.6 mm.  $N = 11.51$ .

$C_{12}H_{11}N_3, 9\frac{1}{2}H_2O$  requires  $N = 11.41$  per cent.

On drying in the water-oven, the crystals become opaque. At this temperature, the loss of weight is about 23—24 per cent.

(I) 0.8932 lost 0.2127 = 23.81 per cent. (II) 0.2634 lost 0.0624 = 23.69 per cent. Mean loss = 23.75 per cent.

The weight remains constant when this degree of dehydration has been reached. The dried substance at this temperature therefore contains 22.72 per cent. of  $H_2O$ , and thus retains between 3 and  $3\frac{1}{2}$  mols.;  $C_{12}H_{11}N_3, 9\frac{1}{2}H_2O$  contains 46.47 per cent. of  $H_2O$ ;  $C_{12}H_{11}N_3, 3\frac{1}{2}H_2O$  contains 24.2 per cent. of  $H_2O$ ;  $C_{12}H_{11}N_3, 3H_2O$  contains 21.5 per cent. of  $H_2O$ .

No further loss takes place at 110—120°. At 120—130°, a further loss of 2.77 per cent. was incurred, and as the compound showed signs of decomposition at this stage, the drying was discontinued and an analysis made.

0.0836 gave 13.25 c.c. moist nitrogen at 14.9° and 766.7 mm.  $N = 18.72$ .

$C_{12}H_{11}N_3, 1\frac{1}{2}H_2O$  requires  $N = 18.75$  per cent.

Although the base is so readily soluble in water when liberated from its salts in aqueous solution, the crystals when once formed dissolve but slowly, even in boiling water. It dissolves slowly in boiling ethyl alcohol, and the saturated solution deposits the base in the form of ochreous, brown, transparent prisms which show the following

\* This decomposition point, redetermined by reference to a short-stemmed thermometer standardised in Berlin, is 288—290°. The absence of acid radicles from the crystals was proved by qualitative examination.



characters when heated in a capillary tube: they soften at 82—85° harden and become opaque at 173—175°, and begin to decompose at 258°; decomposition with blackening is complete at 280°.

A specimen dried in the air at the ordinary temperature was analysed with the following results:

0.1100 gave 14.85 c.c. moist nitrogen at 13° and 766.4 mm. N = 16.06.  
 0.1735 „ 23.1 c.c. „ „ 10.7° „ 759.1 mm. N = 15.86.

This corresponds with a hydrate containing  $3\frac{1}{2}$  mols. of water which requires 16.15 per cent. of nitrogen. The crystals thus obtained do not appear to contain alcohol of crystallisation; no appreciable loss takes place on drying in the water-oven.

The base dissolves also in boiling amyl alcohol, from which it separates on cooling in the form of small, ochreous scales which begin to soften at 150°, and decompose finally with charring from 260° to 280°. It is insoluble in benzene and its homologues and dissolves but very slightly in ether, so that this solvent extracts the base from its aqueous solution to a quite inappreciable extent. The picrate was prepared and analysed after successive crystallisations and found to have the indefinite character already assigned to this salt (Trans., 1900, 77, 1162).

#### *Salts of Ethenyltriaminonaphthalene (M. and S.).*

The following salts have been prepared incidentally in the course of the research, chiefly with the object of ascertaining whether any well-marked distinctions were shown by the corresponding salts of the isomeric bases.

*Acetate.*—Prepared from the sulphate by decomposing with barium chloride,\* filtering off the barium sulphate, removing the excess of barium by sodium carbonate and, after filtration, acidifying the solution with acetic acid. It crystallises in silvery scales, has no definite melting point, softens about 170°, and chars about 270°. A specimen dried in the water-oven gave the following result:

0.1228 gave 15.35 c.c. moist nitrogen at 9.2° and 775.1 mm. N = 15.30.  
 $C_{12}H_{11}N_3, C_2H_4O_2, H_2O$  requires N = 15.30 per cent.

*Oxalate.*—Prepared as above from the sulphate. It forms minute, white needles after crystallisation from water. The dry salt becomes reddish on exposure to light and air; after drying in the water-oven, it has no definite melting point, but softens at 205—210° and chars between 235° and 245°.

\* If the sulphate is basified by ammonia or caustic alkali and the solution then acidified with acetic acid, the crystals which separate still contain sulphuric acid.

0.1317 gave 14.55 c.c. moist nitrogen at 14.2° and 762.9 mm.  $N = 13.02$ .

$C_{12}H_{11}N_3, C_2H_2O_4, 2H_2O$  requires  $N = 13.03$  per cent.

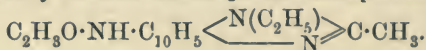
*Mercurichloride*.—Prepared as above from the sulphate, the filtrate, after removal of the barium carbonate, being acidified by hydrochloric acid. On adding mercuric chloride solution, the double salt separates in the form of white scales, which, after drying in the air, have a decomposing point of 238—242°, and on drying in the water-oven lose 4.6 per cent., corresponding approximately with  $1\frac{1}{2}$  mols. of water. The dry salt is anhydrous and decomposes on heating in a capillary tube at 246—249°.

0.1117 gave 7.55 c.c. moist oxygen at 11° and 768.9 mm.  $N = 8.14$ .

0.2553 gave 0.2181 AgCl.  $Cl = 21.12$ .

$C_{12}H_{11}N_3, HCl, HgCl_2$  requires  $N = 8.34$ ;  $Cl = 21.06$  per cent.

*N-Ethyl Derivative of Acetaminoethenyldiaminonaphthalene (M. and S.),*



The replacement of the hydrogen atom of the NH group of the imidazole ring by alkyl radicles destroys the acid character of this ring and gives rise to well-characterised basic compounds, which are more satisfactory to deal with for the purposes of comparison than either the anhydro-bases themselves or their acetyl derivatives. The *N*-methyl derivatives of the acetylated M. and S. base, and of Markfeldt's base, have been described in former communications to the Society (Trans., 1899, 75, 1014; 1900, 77, 1165). As these *N*-alkyl derivatives are of extreme importance in connection with the determination of the constitution of the isomeric bases, their study has been extended and the *N*-ethyl derivatives prepared in the same way as before, namely, by the action of ethyl iodide on the dry *N*-silver salt.

The base thus prepared from the acetyl derivative of the M. and S. base dissolves very readily in all acids, whether organic or inorganic. When liberated from its salts by the addition of alkali to a hot dilute aqueous solution, the base slowly crystallises out on cooling in the form of small, white needles which soften at 188° and melt sharply at 190—191°. By allowing the saturated alcoholic solution to deposit crystals by slow evaporation at the ordinary temperature, the compound is obtained in the form of beautifully defined rhombohedral tablets of a yellowish colour, which are transparent at first, but become opaque on heating and melt sharply at 192—193°.

0.0659 gave 8.65 c.c. moist nitrogen at 19.6° and 767 mm.  $N = 15.17$ .

$C_{16}H_{17}ON_3, \frac{1}{2}H_2O$  requires  $N = 15.22$  per cent.

The base is extremely soluble in alcohol, slightly so in ether, and dissolves somewhat freely in boiling benzene. From the latter solvent it separates in two distinct kinds of crystals. The crop first deposited consists of pale straw-coloured, flat needles grouped into tufts; these are transparent at first, but become opaque on drying without loss of weight. The next crop consists of dense, nodular crystals having an ochreous colour, sometimes mixed with a small quantity of the needle-shaped crystals. The melting point is lower after crystallisation from benzene, the nodules melting at  $184-185^{\circ}$  and the needles less definitely at  $179-181^{\circ}$ . The two kinds of crystals give the same picrate, which is described below, and the composition of the nodular crystals is the same as that of the needles obtained by crystallisation from water.

0.1048 gave 13.9 c.c. moist nitrogen at  $16.5^{\circ}$  and 750.2 mm.  $N = 15.21$ .  
 0.1027 „ 13.55 c.c. „ „  $21.5^{\circ}$  „ 769.3 mm.  $N = 15.15$ ,  
 0.0987 „ 13.15 c.c. „ „  $22.6^{\circ}$  „ 768.9 mm.  $N = 15.20$

The supply of needle-shaped crystals was unfortunately exhausted without our being able to arrive at a definite result concerning their composition, but one analysis indicates that these may consist of the anhydrous base.

0.0394 gave 5.3 c.c. moist nitrogen at  $19.3^{\circ}$  and 767.3 mm.  $N = 15.58$ .  
 $C_{16}H_{17}ON_3$  requires  $N = 15.73$ .

The needles are always less in quantity than the nodules. The fact that the two kinds of crystals give identical picrates indicates that the difference in crystalline form is not due to structural isomerism.

The *picrate* separates out in the form of yellow needles on mixing alcoholic solutions of the base and picric acid. After repeated crystallisation from boiling alcohol, this salt melts sharply with decomposition at  $243-244^{\circ}$ . The unethylated acetyl derivative does not form a picrate (Trans., 1900, 77, 1164).

0.1141 gave 16.15 c.c. moist nitrogen at  $16^{\circ}$  and 754.4 mm.  $N = 16.34$ .  
 0.1056 „ 14.95 c.c. „ „  $19.5^{\circ}$  „ 763.4 mm.  $N = 16.29$ .

$C_{16}H_{17}ON_3 \cdot C_6H_5(NO_2)_3 \cdot OH, H_2O$  requires  $N = 16.37$  per cent.

The hydrochloride gives no precipitate with platinic chloride.

The *aurichloride* separates on mixing solutions of the hydrochloride of the base and auric chloride. It is resinous at first, but slowly changes into a granular, ochreous powder. When dried at the ordinary temperature under a desiccator, it softens at  $90^{\circ}$  and fuses to a red oil at  $180-187^{\circ}$  with decomposition.

0.2436 gave 0.0745 Au = 30.59.

$C_{16}H_{17}ON_3 \cdot HAuCl_4 \cdot 2H_2O$  requires Au = 30.65 per cent.



We may add that the aurichlorides have generally, throughout the present investigation, proved to be of great value for characterising the anhydro-bases of this series.

*Ethenyldiaminonaphthalene (Methylnaphthimidazole) from Ethenyl-triaminonaphthalene (M. and S.).*

In order to eliminate the amino-group from the aminoamidine, the freshly precipitated and moist sulphate was diazotised by adding sodium nitrite in small quantities to the well-cooled, pasty mass until a clear solution was obtained. It is necessary to diazotise in presence of an excess of sulphuric acid in order to avoid the formation of a coloured aminoazo-compound. The solution of the diazonium salt was poured into a large volume of absolute alcohol and the decomposition effected in the usual way, first by warming gently and then by boiling for some hours in a flask with a reflux condenser until nitrogen ceased to be evolved. After distilling off the excess of alcohol, &c., the residual solution was diluted with water and just neutralised with ammonia, when the crude base separated out in a crystalline form as the solution cooled. The base is also acid in character, owing to the NH group of the amidine ring, and advantage was taken of this property for the purification of the compound. The crude product was dissolved in hot dilute sodium hydroxide solution, the solution filtered, and the filtrate made strongly acid with hydrochloric acid. The hydrochloride of the base is but slightly soluble, especially in presence of excess of hydrochloric acid, and separates on cooling in the form of small, white needles. The base can be obtained by suspending the hydrochloride in ammonium carbonate solution and washing the residual crystals on a filter with water until free from soluble salts.

This ethenyldiaminonaphthalene is sparingly soluble in boiling alcohol, from which solvent it separates on cooling in the form of silvery scales. In dealing with large quantities of the base, the best solvent is aniline, which dissolves the compound freely when hot and deposits it in the form of ochreous scales on cooling. We satisfied ourselves by a preliminary experiment that the base is not decomposed or acted on in any way by boiling with aniline. The crystalline deposit can be washed with cold aniline to remove the mother liquor, and finally with cold alcohol until free from aniline. A specimen thus prepared was analysed with the following results:

0.0985 gave 0.2611 CO<sub>2</sub> and 0.0492 H<sub>2</sub>O. C = 72.28; H = 5.55.  
 0.1147 „ 13.55 c.c. moist nitrogen at 10.8° and 769 mm. N = 14.21.  
 0.0995 „ 11.75 c.c. „ „ 13.5° „ 768 mm. N = 14.06.

From these numbers, it appears that the base retains water, as is so generally the case with the compounds dealt with in the course of

these researches. The formula  $C_{12}H_{10}N_2 \cdot H_2O$  requires  $C=72$ ;  $H=6$ ;  $N=14$  per cent. The water could not be expelled by heat without decomposition of the substance. A specimen heated in a U-tube at  $227^\circ$  in a current of dry air lost less than half a molecule of water, namely, 4.2 instead of 4.5 per cent., and then showed signs of decomposing.

The melting point of the base is difficult to determine, as it darkens at about  $258^\circ$  and does not completely fuse until  $264^\circ$ . It is but very slightly soluble in benzene or toluene, but dissolves more freely in boiling amyl alcohol. It separates slowly and imperfectly from its solutions in the alcohols, even when the latter are saturated at their boiling points. The separation from aniline is more complete. The properties of the base and of its salts show that it is isomeric with the ethenyl-diaminonaphthalene described by Prager (*Ber.*, 1885, 18, 2161). The solution of the hydrochloride gives no precipitate with platinic chloride. The base undergoes no change by heating in a sealed tube to  $205^\circ$  with excess of strong hydrochloric acid.

*Hydrochloride.*—A specimen of this salt was prepared by dissolving the base in alcohol with the addition of a little hydrochloric acid and adding an excess of strong hydrochloric acid to the hot solution. The salt separates out on cooling in the form of white needles. After being collected, washed with alcohol containing a little hydrochloric acid, and dried at the ordinary temperature, first in the air and then over lime in a desiccator, the following analytical results were obtained:

0.1012 gave 9.3 c.c. moist nitrogen at  $11^\circ$  and 773 mm.  $N=11.13$ .

0.2993 „ 0.1804 AgCl.  $Cl=14.92$ .

$C_{12}H_{10}N_2 \cdot HCl \cdot H_2O$  requires  $Cl=15.0$ ;  $N=11.41$  per cent.

On attempting to drive off the water by drying at  $100^\circ$ , hydrogen chloride is also expelled, as the basic character of the compound is but feeble.

*Chromate.*—A concentrated solution of the base in dilute acetic acid, on being mixed with a solution of potassium chromate, gives at first an ochreous, gelatinous precipitate which slowly becomes crystalline. If the solutions are dilute, the chromate separates more slowly and appears in the form of ochreous needles. The salt, after being collected, washed with water, drained, and dried in the water-oven, blackens between  $138^\circ$  and  $146^\circ$ ; it has no distinct melting point.

0.1120 gave 10.15 c.c. moist nitrogen at  $12.4^\circ$  and 771.4 mm.  $N=10.89$ .

0.2217 „ 0.0328  $Cr_2O_3$ .  $Cr=10.13$ .

$C_{12}H_{10}N_2 \cdot H_2CrO_4 \cdot 2H_2O$  requires  $N=10.83$ ;  $Cr=10.05$  per cent.

*Picrate.*—On mixing a strong alcoholic solution of the base with an alcoholic solution of picric acid, this salt separates out in the form

of yellow needles. After crystallisation from alcohol, the melting point is  $220^{\circ}$ , with partial sublimation at  $200^{\circ}$ .

0.0995 g. gave  $14.4$  c.c. moist nitrogen at  $13.6^{\circ}$  and  $755.3$  mm.  $N = 16.93$ .

0.1055 „  $15.05$  c.c. „ „  $10^{\circ}$  „  $773.0$  mm.  $N = 17.35$ .

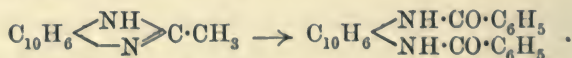
$C_{12}H_{10}N_2, C_6H_2(NO_2)_3OH$  requires  $N = 17.07$  per cent.

*Benzoylation of the Base.*—Benzoyl chloride acts only imperfectly on the base in presence of alkali according to the well-known method of Schotten and Baumann, a product being obtained which could only be partially purified by crystallisation from boiling toluene, in which the unaltered base dissolves but slightly. The hot solution, after filtration to remove the undissolved, unchanged base, was allowed to evaporate spontaneously at the ordinary temperature. A crystalline deposit was thus obtained, which consisted of a mixture of small, nodular tufts of opaque, white needles and large, transparent, brown prisms. The white needles proved to be unaltered ethenyl-diaminonaphthalene. The brown prisms, after being freed from the admixed crystals, were washed with benzene and allowed to dry in the air. The melting point was  $130^{\circ}$ , but softening took place at  $80-90^{\circ}$ . The properties of this compound point to its being a dibenzoyl derivative of *o*-naphthylenediamine.

0.1914 g. gave  $11.6$  c.c. moist nitrogen at  $10.5^{\circ}$  and  $763$  mm.  $N = 7.27$ .

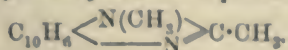
$C_{24}H_{18}O_2N_2$  requires  $N = 7.66$  per cent.

Owing to the difficulty of preparing the new base in large quantity and the imperfect action of benzoyl chloride, we had but very little material to deal with, so that this part of the work must be repeated. It may be pointed out, however, that a breaking down of the amidine ring under the influence of benzoyl chloride and alkali would give rise to dibenzoylnaphthylenediamine:



Similar observations have been recorded in the benzene series by Bamberger and Berlé (*Annalen*, 1893, 273, 342). On the other hand, this rupture of the amidine ring under these conditions does not always occur, as we have found in the case of Markfeldt's ethenyltriaminonaphthalene and as has also been found by Otto Fischer in studying other anhydro-bases of this series (*Ber.*, 1901, 34, 932).



*N-Methyl Derivative of Ethenyldiaminonaphthalene (New Isomeride).*

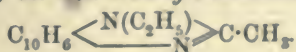
This derivative was prepared by the action of methyl iodide on the dry silver salt according to the method previously described (Trans., 1899, 75, 1013). The *N*-silver salt is immediately precipitated on adding a solution of silver nitrate in dilute alcohol to a solution of the amidine in alcohol containing ammonia. The salt is amorphous and no attempt was made to analyse it. After being collected, washed, and dried, the finely powdered salt was digested for some hours with methyl iodide dissolved in methyl alcohol. After filtration to remove the silver iodide, the alcohol and excess of methyl iodide were evaporated off and the base purified by repeated extraction with dilute acid and precipitation by sodium hydroxide solution. This treatment was made necessary by the fact that methylation is always very incomplete by this method, the product containing much unaltered base, which is removed by the alkali by virtue of its acid character. The pure methyl derivative was obtained as an oil which did not solidify when left for some time. The isomeric *N*-methyl derivative obtained by methylating Prager's ethenyldiaminonaphthalene melts at 143—144° (Otto Fischer, *Ber.*, 1901, 34, 935).

The compound, as might be expected after replacement of the hydrogen of the NH group, no longer possesses any acid characters, but is strongly basic, dissolving at once in all acids, mineral and organic. No well-characterised salts with mineral acids could be prepared with the small quantity of material at our disposal, so the base was converted into picrate by mixing its hot alcoholic solution with an alcoholic solution of picric acid. The salt thus formed crystallises from alcohol in groups of ochreous needles or from dilute solutions in fern-like leaflets with serrated edges. The melting point is 228°, with partial sublimation at 201°. A specimen dried in the water-oven was analysed with the following results:

0.0954 gave 13.2 c.c. moist nitrogen at 12.5° and 762 mm. N = 16.42.

0.1037 „ 14.4 c.c. „ „ 12.4° „ 760 mm. N = 16.43.

$\text{C}_{13}\text{H}_{12}\text{N}_2\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$  requires N = 16.47 per cent.

*N-Ethyl Derivative of the New Ethenyldiaminonaphthalene,*

This compound was prepared from the dry silver salt and ethyl iodide in the same way as the methyl derivative. After purification by repeated solution in dilute acid and precipitation by excess of

sodium hydroxide, the base was obtained as a viscid oil which solidified slowly when left undisturbed, or more rapidly by rubbing it against the sides of the beaker with a glass rod. The base separates as an oil from methyl or ethyl alcohol and from acetone. It dissolves in boiling benzene and separates on cooling in the form of transparent ochreous plates. The melting point is  $84^{\circ}$  with previous softening.

0.0644 gave 7.2 c.c. moist nitrogen at  $13.5^{\circ}$  and 759.5 mm.  $N = 13.16$ .

0.0967 „ 11.1 c.c. „ „ „  $13.4^{\circ}$  „ 765 mm.  $N = 13.61$ .

$C_{14}H_{14}N_2$  requires  $N = 13.3$  per cent.

As in the case of the unalkylated amidines, the salts proved to be more satisfactory for analytical and diagnostic purposes.

*Chromate*.—On adding a solution of potassium chromate to a solution of the hydrochloride of the base, an oily chromate separates, and this slowly solidifies to a pulp of ochreous needles. The salt, after drying in the water-oven, softens at  $165^{\circ}$  and decomposes at about  $175^{\circ}$ .

0.2051 gave 0.0459  $Cr_2O_3$ .  $Cr = 15.32$ .

0.1238 „ 9.05 c.c. moist nitrogen at  $15^{\circ}$  and 746.4 mm.  $N = 8.40$ .

$C_{14}H_{14}N_2 \cdot H_2CrO_4$  requires  $Cr = 15.87$ ;  $N = 8.55$  per cent.

*Picrate*.—This salt separates in the form of yellow needles on mixing alcoholic solutions of the base and of picric acid. After two crystallisations from alcohol and drying in the water-oven, the salt melts with decomposition at  $234-235^{\circ}$ .

0.1269 gave 16.3 c.c. moist nitrogen at  $13.7^{\circ}$  and 768.4 mm.  $N = 15.29$ .

0.1274 „ 16.25 c.c. „ „ „  $13^{\circ}$  „ 771.4 mm.  $N = 15.28$ .

$C_{14}H_{14}N_2 \cdot C_6H_2(NO_2)_3 \cdot OH \cdot H_2O$  requires  $N = 15.34$  per cent.

*Aurichloride*.—On mixing solutions of the hydrochloride of the base and of auric chloride, a precipitate consisting of minute, ochreous needles separates out. An attempt to dry the salt in the water-oven showed that it had a low melting point, so a specimen was dried at the ordinary temperature under a desiccator and then analysed.

0.2986 gave 0.10  $Au = 33.49$  per cent.

0.1374 „ 5.5 c.c. moist nitrogen at  $13.7^{\circ}$  and 758.9 mm.  $N = 4.71$ .

$C_{14}H_{14}N_2 \cdot HAuCl_4 \cdot 2H_2O$  requires  $Au = 33.63$ ;  $N = 4.79$  per cent.

Some of the hydrated salt was dried in a porcelain crucible in the water-oven until constant in weight.

0.2817 lost  $0.0088 = 3.12$  per cent.

0.2074 „  $0.0066 = 3.18$  „

The latter, after drying = 0.2008, gave 0.0699  $Au = 34.81$ .

$C_{14}H_{14}N_2 \cdot HAuCl_4 \cdot H_2O$  requires  $Au = 34.70$ ;  $H_2O = 3.17$  per cent.

The existence of hydrates containing one and two molecules of water respectively having been established by the foregoing analyses, an attempt was made to expel the last molecule by drying at a higher temperature. At  $120^{\circ}$ , the loss was greater than is required by theory for two molecules of water, namely, 7.77 and 7.97 (in two determinations) instead of 6.12, so that, at this temperature, the decomposition proceeds further than mere dehydration. The original (hydrated) aurichloride is soluble in alcohol, and is precipitated on diluting the solution with water as a red oil, which slowly solidifies to a crystalline mass. The melting point is  $113^{\circ}$  with previous softening. When heated to its melting point, the salt fuses to a red oil, which solidifies but slowly when cold.

*Platinichloride*.—This salt separates in the form of small, ochreous scales on mixing solutions of the hydrochloride of the base and of platinic chloride. A specimen dried in a desiccator at the ordinary temperature furnished the following results :

0.1600 gave 0.0344 Pt = 21.5.

$2C_{14}H_{14}N_2, H_2PtCl_6, 4H_2O$  requires Pt = 21.59 per cent.

0.4838 dried in the desiccator and heated till constant in the water-oven lost  $0.0196 = 4.05$  per cent. This corresponds with a loss of two molecules of water.

$2C_{14}H_{14}N_2, H_2PtCl_6, 4H_2O - 2H_2O$  requires a loss = 4.0 per cent.

The above specimen, dried at  $100^{\circ}$ , furnished the following results :

0.2999 gave 0.0672 Pt = 22.41 per cent.

0.0972 „ 5.45 c.c. moist nitrogen at  $14.5^{\circ}$  and 762.7 mm. N = 6.59.

$2C_{14}H_{14}N_2, H_2PtCl_6, 2H_2O$  requires Pt = 22.49 ; N = 6.48 per cent.

The hydrate containing two molecules of water undergoes a further loss of one molecule when heated in an air-bath to  $130^{\circ}$ .

0.3667 lost 0.0074  $H_2O = 2.02$ .

$2C_{14}H_{14}N_2, H_2PtCl_6, 2H_2O - H_2O$  requires a loss = 2.08 per cent.

The above monohydrate gave the following results :

0.1992 gave 0.0459 Pt = 23.04.

0.1100 „ 6.7 c.c. moist nitrogen at  $17.8^{\circ}$  and 755.6 mm. N = 6.98.

$2C_{14}H_{14}N_2, H_2PtCl_6, H_2O$  requires Pt = 22.99 ; N = 6.62 per cent.

Dehydration could not be carried further without decomposing the salt. The hydrate obtained by drying in the water-oven (containing two molecules of water) has a decomposing point of about  $232-236^{\circ}$ . The existence of three definite hydrates containing one, two, and four molecules of water respectively is established by these results.



The *mercurichloride* separates on mixing solutions of the hydrochloride of the base and of mercuric chloride. It is oily at first, but slowly solidifies to a mass of white needles. The analytical results did not lead to any definite formula, but the examination of this salt will be carried further when more of the *N*-ethyl derivative has been prepared.

*Comparative Study of the Isomeric Ethenyldiaminonaphthalenes.*

The only anhydro-base of this composition hitherto described is that which we have associated with the name of Prager (*Ber.*, 1885, 18, 2161). It has already been stated in a former paper (Meldola and Eynon, *Trans.*, 1900, '77, 1170) that the replacement of the  $\text{NH}_2$  group by hydrogen in Markfeldt's ethenyltriaminonaphthalene apparently gave rise to the formation of Prager's ethenyldiaminonaphthalene. This observation we are now enabled to confirm, having repeated the experiment on a larger scale, and made a further study of the product. The *N*-methyl derivative of this ethenyldiaminonaphthalene has been recently described by Otto Fischer (*Ber.*, 1901, 34, 935), to whom we are indebted for specimens of the base, which he was good enough to send at our request for the purpose of comparing with our own preparations. The melting point is 143—144°.

The base used in the present investigation was prepared by the reduction of  $\alpha$ -nitro- $\beta$ -acetophthalide according to the method of Liebermann and Jacobson (*Annalen*, 1882, 211, 67), this method, after we had established the identity of Prager's base with that obtained from Markfeldt's ethenyltriaminonaphthalene, having been found to be the most convenient. We have proved incidentally that  $\alpha$ -nitro- $\beta$ -acetophthalide gives the same anhydro-base, whether reduced by tin and hydrochloric acid or by iron and hydrochloric acid.

To the properties of the base, as described in previous papers by other investigators, we can make the following additions and corrections.

The melting point of the pure picrate is 253—254°, as corrected by reference to the short-stemmed standard thermometer having the Berlin certificate. Softening takes place before actual fusion, so that the melting point assigned by Lellmann and Remy, 242° (*Ber.*, 1886, 19, 801) is probably the softening point. The compound is sufficiently acid to form a silver salt, which is precipitated in a gelatinous form on mixing an alcoholic solution of the base with an ammoniacal solution of silver nitrate. This *N*-silver salt, when dry, can be used for the preparation of the *N*-alkyl derivatives, but the yield by this method is not so good as when the alkylation is effected by heating the base with an alcoholic solution of the alkyl iodide.

The *chromate* is precipitated in the form of minute, ochreous needles on mixing solutions of the acetate of the base and potassium chromate. After being collected, washed with water, and dried at  $100^{\circ}$ , the following results were obtained:

0.3869 gave 0.0992  $\text{Cr}_2\text{O}_3$ . Cr = 17.55.

0.1236 „ 9.6 c.c. moist nitrogen at  $9.5^{\circ}$  and 772.5 mm. N = 9.46.

$\text{C}_{12}\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{CrO}_4$  requires N = 9.35; Cr = 17.35 per cent.

This chromate has no definite melting or decomposing point. The *N-methyl* derivative was prepared by the action of methyl iodide on the dry *N-silver* salt in the usual way, and also by heating the base with methyl iodide and methyl alcohol in a sealed tube (Otto Fischer, *Ber.*, 1901, 34, 935). The *picrate* of this base separates from alcohol in rosettes of yellow needles. The melting point is  $227-228^{\circ}$ , so that the difference between the melting points of the picrates of the isomeric bases is comparatively trifling. A more detailed study of the *N-ethyl* derivative was accordingly undertaken.

#### *N-Ethyl Derivative of Prager's Ethenyldiaminonaphthalene.*

This base was most conveniently prepared by the direct alkylation of the amidine by heating with one molecular proportion of ethyl iodide dissolved in alcohol in a sealed tube in a water-bath. The ethylation of the *N-silver* salt gives the same base, but the yield is not so good, a large proportion of the amidine escaping the action of the alkyl iodide. The free base, liberated from the hydriodide (which separates out in the form of white needles when the contents of the tube are cold) and purified by repeated solution in dilute acid and precipitation by sodium hydroxide, has hitherto only been obtained in the form of a viscid resin. It forms a hydrochloride,  $\text{C}_{14}\text{H}_{14}\text{N}_2\cdot\text{HCl}$ , which crystallises out slowly in white needles when an excess of strong hydrochloric acid is added to a strong solution of the hydrochloride.

*Chromate*.—On mixing solutions of potassium chromate and of the acetate of the base, the chromate separates at once in minute, ochreous needles. After drying in the water-oven, the salt decomposes at  $199-203^{\circ}$ .

0.1105 gave 0.0264  $\text{Cr}_2\text{O}_3$ . Cr = 16.36.

0.0947 gave 7.25 c.c. moist nitrogen at  $12.1^{\circ}$  and 749.1 mm. N = 8.93.

$\text{C}_{14}\text{H}_{14}\text{N}_2\cdot\text{H}_2\text{CrO}_4$  requires Cr = 15.87; N = 8.55 per cent.

*Picrate*.—This salt crystallises from alcohol in yellow needles melting at  $248^{\circ}$ .

0.0595 gave 8.15 c.c. moist nitrogen at  $15.6^{\circ}$  and 752.7 mm.  $N = 15.82$ .

$C_{14}H_{14}N_2 \cdot C_6H_2(NO_2)_3 \cdot OH$  requires  $N = 15.97$  per cent.

*Platinichloride*.—This salt is precipitated as a micro-crystalline, ochreous powder on mixing solutions of the hydrochloride of the base and of platinic chloride. After being collected, washed, and dried in the water-oven, the following results were obtained:

0.3342 gave 0.0782 Pt = 23.40.

0.1334 gave 7.3 c.c. moist nitrogen at  $13.9^{\circ}$  and 769.5 mm.  $N = 6.52$ .

$2(C_{14}H_{14}N_2) \cdot H_2PtCl_6$  requires Pt = 23.47;  $N = 6.77$  per cent.

*Aurichloride*.—On mixing solutions of the hydrochloride and of auric chloride, a dense, ochreous, micro-crystalline precipitate is formed. On drying in the water-oven, this salt becomes anhydrous.

0.2893 gave 0.1038 Au = 35.88.

$C_{14}H_{14}N_2 \cdot HAuCl_4$  requires Au = 35.84 per cent.

The salt fuses to a reddish oil under boiling water. It dissolves in alcohol, and is precipitated by water in the form of minute, ochreous needles. The dry salt, when heated in a capillary tube, begins to shrink at about  $142^{\circ}$ ; between  $145^{\circ}$  and  $152^{\circ}$ , it gradually becomes resinous and red in colour, and at  $230^{\circ}$  decomposition with the evolution of gas takes place.

#### *Salts and Derivatives of Markfeldt's Ethenyltriaminonaphthalene.*

In addition to the salts and derivatives of this base described in former papers, the following have been prepared for the purpose of bringing out any further characters which might serve to distinguish the isomerides.

The *oxalate* is prepared by boiling the free base with dilute oxalic acid solution; it crystallises out in nodular rosettes of white needles which become pink on exposure to the air. The air-dried salt was analysed.

0.0955 gave 9.55 c.c. moist nitrogen at  $14.6^{\circ}$  and 768.1 mm.  $N = 11.85$ .

0.0551 „ 5.5 c.c. „ „  $15.4^{\circ}$  „ 768 mm.  $N = 11.78$ .

$C_{12}H_{11}N_3 \cdot C_2H_2O_4 \cdot 4H_2O$  requires  $N = 11.72$  per cent.

The salt undergoes no appreciable loss on heating in the water-oven. At a higher temperature, it becomes coloured, owing either to oxidation or to some interaction which occurs between the base and acid.

*Mercurichloride*.—This salt, prepared by mixing solutions of the hydrochloride of the base and of mercuric chloride, consists of white needles which become red on keeping. It has no definite melting point, but decomposes at about  $280^{\circ}$ .



0.1079 gave 5.9 c.c. moist nitrogen at 13.8° and 773.9 mm. N = 6.55.  
 0.1307 „ 6.95 c.c. „ „ 15.7° „ 770.6 mm. N = 6.34.  
 0.3762 „ 0.3435 AgCl. Cl = 22.57.  
 0.1418 „ 0.1297 AgCl. Cl = 22.61.

$C_{13}H_{11}N_3 \cdot 2HCl, HgCl_2, 5H_2O$  requires N = 6.67; Cl = 22.46 per cent.

The salt only lost 0.44 per cent. at 100°. At higher temperatures, it becomes coloured by oxidation.

*Benzoyl Derivative.*—This compound was briefly described in the last paper (Trans., 1900, 77, 1165), but as its melting point is practically the same as that of its isomeride (Trans., 1899, 75, 1015) it was considered desirable to make a further examination of the product of benzoylation of Markfeldt's base under different conditions. The benzoyl derivative was originally prepared by the action of benzoyl chloride on the hydrochloride of the base in the presence of sodium benzoate (Trans., 1900, 77, *loc. cit.*). We have therefore prepared for comparison a specimen of the benzoyl derivative by the Schotten-Baumann method. The two products proved to be identical, so that no disruption of the amidine ring takes place under the influence of benzoyl chloride in presence of alkali; the amino-group in the amino-amidines of this series thus appears to protect the ring in question. The breaking down of the amidine ring under the conditions named would give rise to tribenzoyltriaminonaphthalene, but the analyses prove that this compound is not formed.

The benzoyl derivative of Markfeldt's base is more basic and less acid than its isomeride. A specimen was prepared for analysis by crystallisation from amyl alcohol. The crystals, consisting of dense, white prisms, were washed with ethyl alcohol and finally dried at 180° to ensure expulsion of any retained traces of the solvent.

0.1043 gave 0.2911  $CO_2$  and 0.0464  $H_2O$ . C = 76.13; H = 4.94.

0.1014 „ 12 c.c. moist nitrogen at 10° and 762 mm. N = 14.19.

These results agree with the formula of a monobenzoyl derivative,



which requires C = 75.75; H = 4.98; N = 13.95 per cent.

An attempt to prepare the *N*-ethyl derivative of the acetyl derivative of Markfeldt's base by the action of ethyl iodide on the dry silver salt led to a negative result, the unchanged acetyl derivative being recovered after the operation. The experiment may be worth repetition, but the result shows that there is a marked difference in the behaviour of the isomerides so far as concerns the facility with which the hydrogen of the NH group can be replaced by alkyl radicles.

*Conversion of Ethenyltriaminonaphthalene (M. and S.) into its Isomeride (Markfeldt's).*

Some of the sulphate was suspended in alcohol, basified by sodium hydroxide, and then converted into hydrochloride by the addition of hydrochloric acid. The alcoholic solution of the hydrochloride was boiled for some hours in a flask with a reflux condenser with iron filings and hydrochloric acid, fresh portions of iron and acid being added from time to time so as to insure a continuous reducing action, as in the process originally given by Markfeldt for the preparation of his ethenyltriaminonaphthalene (*Ber.*, 1898, 31, 1174). After distilling off the alcohol, the solution was filtered and acidified with excess of sulphuric acid. The sulphate, which crystallised out on cooling, was purified by crystallisation from water and gave Markfeldt's amino-amidine on basification. This was proved by the melting point of the hydrate (84—85°) and of the anhydrous base (135—136°), as well as by conversion into the phenylazo-compound of m. p. 223—224° (Meldola and Eynon, *Trans.*, 1900, 77, 1160, 1167).\*

This result appeared to suggest that Markfeldt's base might be the final product of reduction of our (M. and S.) base and that the latter was the first stage of the reduction of dinitro- $\alpha$ -acetophthalide. In order to test this point, some dinitro- $\alpha$ -acetophthalide was reduced in alcohol with iron and hydrochloric acid in the usual way, only instead of continuing the reduction by heating with iron and acid for some hours, as in Markfeldt's process, the operation was stopped as soon as reduction was complete, as indicated by the disappearance of the dinitro-compound owing to its passing into solution as aminoamidine. The solution, on filtration, removal of the alcohol by evaporation, and isolation of the amidine as sulphate, gave Markfeldt's compound, so that prolonged reduction is not essential for the production of this modification. Whether the action of iron is specific or whether other metals of the iron group give the same result must be determined by further investigation. One experiment has been made in which 2:4-dinitro- $\alpha$ -acetophthalide was reduced in the usual way with zinc and hydrochloric acid. In this case, the sulphate of our (M. and S.) base was obtained. Another experiment with 5 per cent. sodium amalgam proved that the M. and S. base does not undergo isomeric transformation under the influence of this reducing agent. Some of our sulphate was suspended in alcohol and boiled for 7—8 hours with an excess of the amalgam, the solution being kept slightly acid by the occasional addition of dilute acetic acid. The suspended sulphate, on being basi-

\* The melting point given in the former paper, namely, 220—221°, was unchecked by reference to the short-stemmed standard thermometer.

fied by the sodium, at once dissolves, so that the experimental conditions may be described as the action of sodium amalgam on the acetate of the base in presence of acetic acid. The sulphate recovered after this treatment proved, as already stated, to be that of the unchanged base. This was shown by its ready solubility in water and by the formation of the characteristic phenylazo-compound.

The conditions determining the isomeric change in this remarkable and apparently unique case will be made the subject of further inquiry when the constitutional formulæ have been definitely proved. We may add that the reverse change, namely, Markfeldt's into the isomeric (M. and S.) aminoamidine has not yet been found possible. The possibility of one form being a polymeride of the other has also been kept in mind, but no compounds suitable for the determination of the molecular weight had been obtained until the experiments described in this paper were carried out. The *N*-alkyl derivatives of the amidines seem well adapted for this purpose as they are sufficiently soluble in benzene and are free from attached or combined water.

The expenses incurred in connection with this research have been partly met by a grant from the Government Grant Fund of the Royal Society. We desire also to acknowledge the assistance given by the "Badische Anilin- und Soda-Fabrik" of Ludwigshafen and by Messrs. Leopold Cassella and Co. of Frankfort, these firms having kindly supplied us with some of the raw materials required for the investigation.

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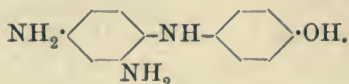
## CXVII.—*Polythiosulphonic Acids of p-Diamines.*

By ARTHUR GEORGE GREEN and ARTHUR GEORGE PERKIN.

SINCE the discovery of Vidal black in 1896, a large class of colouring-matters has become known, the members of which are obtained by heating aromatic compounds of the most varied nature with the sodium polysulphides. The dyestuffs of this class, which are known as "Sulphur" or "Sulphide" colours, vary in shade from black and brown to blue, dark green, and dull yellow. They possess in common certain characteristic properties. They are insoluble in water, but dissolve in a solution of sodium sulphide. From this solution, which appears to contain the dyestuff in a reduced or "leuco" condition, unmordanted cotton is dyed directly, the shades obtained being remark-



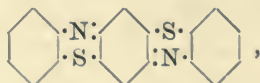
able for their extreme fastness to washing, light, and dilute acids. The most important members of the class are those which dye black shades, and these are now employed in very large quantities in cotton dyeing. These black dyestuffs are obtained by heating with sodium sulphide and sulphur various aminohydroxy-derivatives of diphenylamine, such, for instance, as diaminohydroxydiphenylamine,



In spite of the commercial importance which these colouring matters have attained, it is remarkable that at present very little is known regarding their constitution.

Five years since, one of the authors of this communication commenced a long investigation on sulphide blacks with the hope of discovering a synthetical method for their preparation which would give an indication of their constitution, and at the same time form the basis of a less empirical process for their manufacture. This investigation, the results of which are recorded in the specifications of English patents numbered 21832 of 1898, 22460 of 1898, 22847 of 1898, 5039 of 1899, 18658 of 1899, and 4792 of 1900, was carried out in the laboratory of the Clayton Aniline Co., Manchester, in collaboration with A. Meyenberg.\*

Starting from the view expressed by Raymond Vidal that the sulphide blacks should be regarded as polythiazines constituted on the type



attempts were made to synthesise substances of this type in a manner analogous to that employed by A. Bernthsen for the synthesis of methylene blue. Just as Bernthsen obtained the latter by the oxidation of a dimethyl-*p*-phenylenediaminemonothiosulphonic acid with a monamine, so it was thought possible, assuming Vidal's formula to be correct, that the then unknown dithiosulphonic acid of *p*-phenylenediamine would give by oxidation, in the presence of monamines, black colouring matters of the sulphide class. This anticipation was so far substantiated by experiment that, on operating in this manner, a large series of black and brown colouring matters was obtained which possessed the general dyeing properties of sulphide dyestuffs. Contrary to expectation, however, they proved to be chemically distinct from any known members of the sulphide class, from which they

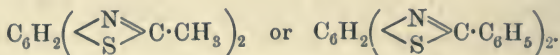
\* To this gentleman and to other chemists of the Clayton Aniline Co. we desire to acknowledge our indebtedness for a portion of the results here described.

differed considerably in their feeble affinity for cotton and their lesser fastness to washing. The cause of this difference still remains unexplained, but there is reason for believing that these new colouring matters derived from polythiosulphonic acids are not, as was at first believed, polythiazines or sulphydro-derivatives of these, but are more probably sulphydro- (SH) or thiosulpho- ( $S\cdot SO_3H$ ) derivatives of insoluble dyestuffs of the aniline black class (complex indamines?). In view of the enormous diversity of the organic compounds (ranging from sawdust and fats to naphthols and derivatives of diphenylamine), which, on reaction with alkaline polysulphides, give rise to sulphide dyestuffs, the view has recently gained ground that it is impossible to attribute the peculiar dyeing properties of these colouring matters to their nucleal structure, and that these properties must be referred to the common presence of the sulphydro-group (SH) in all these (otherwise differently constituted) substances. By virtue of this group, the dyestuff (the parent compound of which is insoluble) is rendered soluble in water containing sodium sulphide, and from such a solution cotton is dyed by the atmospheric oxidation of the soluble  $-SNa$  derivative to the insoluble  $-S-S-$  derivative, just as cotton is dyed with indigo from an alkaline solution of leucindigo. Therefore, in spite of their similar dyeing properties, the products derived from polythiosulphonic acids may have a different nucleal structure to those obtained by the action of alkaline polysulphides on derivatives of diphenylamine, and only share with the latter the common possession of the SH groups. The reaction is capable of the widest possible variations, thus, as described in the above-mentioned patent specifications, not only do the dithio-sulphonic acids of *p*-diamines give rise by oxidation, in the presence of monamines, or with diamines, or with mixtures of such amines and phenols, to dyestuffs of this class, but the latter are also formed in a similar manner from *p*-phenylenediaminetetrathiosulphonic acid.

All these colouring matters, like those obtained by the polysulphide reaction, are black, amorphous powders, incapable of being purified sufficiently for analysis. The intermediate products, however, the polythiosulphonic acids of the *p*-diamines, of which several were obtained in the course of the above investigation, are well-crystallised compounds readily capable of purification.

A further description of some of these interesting compounds and their closer characterisation is the object of the present communication. Up to the present, only monothiosulphonic acids have been described. For the preparation of polythiosulphonic acids of the *p*-diamines, the same method was followed as that used by Bernthsen for obtaining the monothiosulphonic acids, with the exception that a larger molecular proportion of thiosulphate and a corresponding proportion of the oxidising agent were employed. It is remarkable

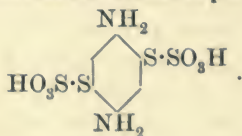
that it is possible in this way to replace the whole of the nuclear hydrogen in *p*-phenylenediamine by  $S \cdot SO_3H$  groups, thus forming a tetrathiosulphonic acid,  $C_6(S \cdot SO_3H)_4(NH_2)_2$ . Owing to the presence of the  $S \cdot SO_3H$  groups in ortho-positions with respect to the amino-groups, the *p*-phenylenediaminedithiosulphonic acid exhibits several characteristic condensations. Thus, with nitrous acid, it gives a stable bisdiazosulphide,  $C_6H_2\left(\begin{smallmatrix} N \\ | \\ S \end{smallmatrix}\right)_2$ , with organic acid anhydrides, or with aldehydes, it gives anhydro-derivatives, thus :



On boiling the dithio- or tetrathio-sulphonic acid of *p*-phenylenediamine with aqueous acids, sulphurous and sulphuric acids are split off, and yellow or red salts of sulphide bases are obtained. These appear to have the formulæ  $C_6H_2(NH_2)_2 \ll S$  and  $S \gg C_6(NH_2)_2 \ll S$ . These bases are of dark colour, insoluble in water and other solvents, but dissolve in an aqueous solution of sodium sulphide, in which respect they resemble the sulphide colours. They are reconverted into the respective polythiosulphonic acids by prolonged treatment with sulphurous acid in presence of air. On reduction with zinc dust, the *p*-phenylenediaminedithiosulphonic acid gives rise to the dihydro-sulphide,  $C_6H_2(NH_2)_2(SH)_2$ .

From the formation of the above condensation products, it must be concluded that in the dithiosulphonic acid each  $S_2O_3H$  group occupies an ortho-position with respect to a different amino-group, and these radicles are therefore probably in the para-position to each other.

*p*-Phenylenediaminedithiosulphonic Acid,



For the preparation of this compound, the following method was found to give the best yields. A solution of 54 grams of *p*-phenylenediamine in 250 c.c. of water and 268 grams of glacial acetic acid was mixed with a large quantity of finely-chopped ice and treated quickly with a slightly alkaline solution of sodium thiosulphate and sodium chromate, prepared by dissolving 133 grams of sodium bichromate in 250 c.c. of water, neutralising with caustic soda, and adding 500 grams of sodium thiosulphate dissolved in 750 c.c. of water. The reaction



mixture was nearly neutralised with caustic soda and 500 grams of potassium chloride were added. After two days, the greenish precipitate, which had separated, was dissolved in boiling water, the solution rendered alkaline with potassium carbonate, filtered from chromium hydroxide, and the filtrate again saturated with potassium chloride. The potassium salt of the dithiosulphonic acid, which crystallised out on cooling, was further purified by recrystallisation from hot water containing potassium carbonate and animal charcoal. The complete removal of the last traces of chromium was difficult, and could only be accomplished by the employment of both these agents together; the yield was 46 grams. The purified salt is obtained in yellow, prismatic needles somewhat readily soluble in water, much less soluble in presence of potassium chloride; it contained water of crystallisation and gave on analysis:

|              | Found. | Calculated for<br>$C_6H_2(NH_2)_2(S_2O_3K)_2 \cdot 2H_2O$ . |
|--------------|--------|---|
| $H_2O$ ..... | 8.9    | 8.1   |
| S .....      | 29.8   | 29.8  |
| K .....      | 17.3   | 17.5  |

From a strong aqueous solution of the potassium salt, acetic acid precipitates an acid potassium salt; hydrochloric acid, on the other hand, yields the free dithiosulphonic acid in nearly colourless, glistening prisms. The latter is easily soluble in water, and contains 2 molecules of water of crystallisation:

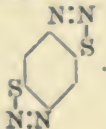
Found  $H_2O = 9.46$ .

Calculated = 9.78.

When dried at  $110^\circ$ , the acid gave on analysis the following numbers:

|            | Found. | Calculated for<br>$C_6H_2(NH_2)_2(S_2O_3H)_2$ . |
|------------|--------|---|
| C .. ..... | 21.88  | 21.68   |
| H .. ..... | 2.55   | 2.41  |

*p*-Phenylenebisdiazosulphide,



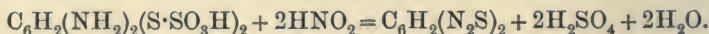
This compound is formed quantitatively by the action of nitrous acid on the dithiosulphonic acid. A cold aqueous solution of the potassium salt, when acidified with acetic acid and treated with a solution of sodium nitrite (2 mols.), yielded a colourless, crystalline precipitate, which was collected and recrystallised from acetic acid.

The product formed colourless, prismatic crystals, sparingly soluble in cold acetic acid; the yield was 44.89 per cent., the calculated amount being 47.54. It melts at 224—226° with decomposition, and slightly above this temperature explodes with some violence. On this account, it was analysed by adding a weighed quantity of sulphuric acid to the substance in the platinum boat.

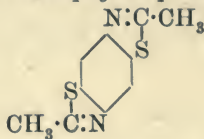
|        | Found. | Calculated for<br>$C_6H_2(N_2S)_2$ . |
|--------|--------|--------------------------------------|
| C..... | 37.11  | 37.11                                |
| H..... | 1.31   | 1.03                                 |
| N..... | 29.11  | 28.87                                |
| S..... | 33.09  | 32.99                                |

An estimation of the amount of sodium nitrite required for the production of this substance from the potassium dithiosulphonate gave 33.52; theory for  $2NaNO_2$ , 33.82 per cent.

The reaction therefore takes place according to the equation :



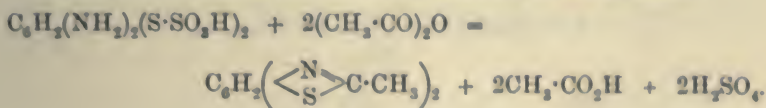
*Diethenyl-2 : 5-disulphydro-p-diaminobenzene,*



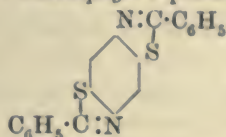
One and a half grams of the dithiosulphonic acid were heated for a few minutes with 15 grams of acetic anhydride and a few drops of sulphuric acid. On pouring the solution into water, a colourless precipitate separated, which was collected and dried. As the elimination of the  $SO_3H$  groups did not seem to be quite complete, the product was heated to 180°, when effervescence occurred, and it lost 10 per cent. in weight. Finally, it was crystallised from alcohol with the addition of animal charcoal. The product forms colourless needles readily soluble in hot alcohol and benzene; it melts at 98—100° and possesses feebly basic properties. On analysis, it gave the following numbers :

|         | Found. | Calculated for<br>$C_6H_2\left(\frac{N}{S}>C\cdot CH_3\right)_2$ . |
|---------|--------|--|
| C ..... | 54.24  | 54.54  |
| H ..... | 4.00   | 3.64   |
| N ..... | 12.83  | 12.72  |
| S ..... | 29.56  | 29.09  |

The compound is therefore formed according to the equation :



*Dibenzoyl-2 : 5-disulphonylhydro-p-diaminobenzene,*

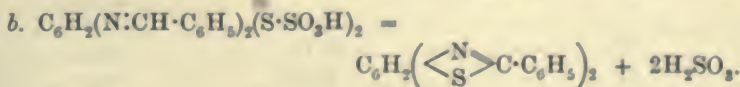
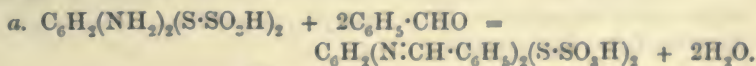


A solution of 1 gram of the potassium dithiosulphonate in 10 c.c. of water was treated with 15 c.c. of acetic acid, and to the boiling solution  $5\frac{1}{2}$  c.c. of benzaldehyde were added. The nearly colourless, crystalline precipitate which separated melted slowly with evolution of gas (from  $185^\circ$  to  $228^\circ$ ), and appeared to contain an admixture of the intermediate product, benzylidenephenylenediaminedithiosulphonic acid. It was therefore heated at  $230-240^\circ$  for about half an hour, and then crystallised from amyl alcohol containing animal charcoal. The product now melted at  $232-234^\circ$  and crystallised in very pale straw-coloured needles. On analysis, it gave the following numbers :

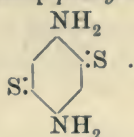
|         | Found. | Calculated for<br>$\text{C}_6\text{H}_2\left(\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}\cdot\text{C}_6\text{H}_5\right)_2$ |
|---------|--------|---|
| C ..... | 69.65  | 69.76   |
| H ..... | 3.14   | 3.48  |
| N ..... | 8.24   | 8.14  |
| S ..... | 18.31  | 18.60   |

If the reaction is allowed to proceed in the cold with the employment of the theoretical proportion of benzaldehyde, the above-mentioned intermediate compound appears to be the chief product, and separates as an orange-coloured precipitate consisting of fine needles.

The reaction probably proceeds, therefore, in two stages :





*2:5-Disulphido-p-phenylenediamine,*

On digesting a boiling solution of the potassium dithiosulphonate with an excess of hydrochloric acid, the solution becomes yellow, sulphurous acid is evolved, and a crystalline precipitate gradually separates; this is collected, washed successively with hydrochloric and acetic acids, and dried at  $100^{\circ}$ . The yield is 93 per cent. of the theoretical, the product consisting of small, yellow needles having the formula  $C_6H_2S_2(NH_2)_2 \cdot 2HCl$  :

|         | Found. | Calculated. |
|---------|--------|-------------|
| C ..... | 30.0   | 29.63       |
| H ..... | 3.57   | 3.27        |
| N ..... | 11.52  | 11.52       |

If sulphuric acid is employed in place of hydrochloric acid, a crystalline sulphate results.

On treating the dihydrochloride with water, it loses hydrochloric acid and is converted into the monohydrochloride; the latter was obtained crystalline in the form of minute, ochre-yellow needles by boiling the dihydrochloride with pyridine.

On analysis, it gave :

|         | Found. | Calculated for<br>$C_6H_2S_2(NH_2)_2 \cdot HCl$ . |
|---------|--------|---|
| C ..... | 34.19  | 34.91   |
| H ..... | 3.29   | 3.33  |

By the action of ammonia on the dihydrochloride, the free base was obtained as a garnet-coloured, amorphous precipitate. By dissolving the dihydrochloride in hot aniline and adding alcohol drop by drop, the base can be obtained in minute, glistening, garnet-red prisms; it melts at  $234-235^{\circ}$  with decomposition, and is soluble in boiling aqueous sodium sulphide to a pale yellow solution. On analysis, it gave the following numbers :

|         | Found. | Calculated for<br>$C_6H_2S_2(NH_2)_2$ . |
|---------|--------|---|
| C ..... | 42.73  | 42.35                                   |
| H ..... | 4.22   | 3.53                                    |
| N ..... | 16.42  | 16.41                                   |
| S ..... | 37.20  | 37.64                                   |

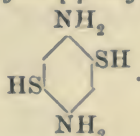
A determination was made of the quantity of sulphurous and sulphuric acids set free on boiling the dithiosulphonic acid with mineral acids.

|                       | Found. | Theory for<br>1 mol. proportion. |
|-----------------------|--------|----------------------------------|
| Sulphurous acid ..... | 19·54  | 20·09                            |
| Sulphuric acid .....  | 24·79  | 24·02                            |

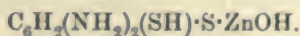
The formation of the disulphide therefore takes place in accordance with the equation :



2:5-Disulphydro-p-phenylenediamine,



This product was obtained by reduction of the dithiosulphonic acid in aqueous solution with zinc dust and hydrochloric acid, additional quantities of the acid and zinc being added from time to time until hydrogen sulphide was no longer evolved. The solution (which on cooling deposited crystals of the hydrochloride of the new base) was filtered hot and treated drop by drop with sodium acetate solution. After filtration from a small quantity of a green impurity, the base was thrown down as a white precipitate by the addition of a further quantity of sodium acetate solution and heated to boiling until it became crystalline. After washing with water and alcohol, the dried product formed small, colourless prisms insoluble in water and alcohol, which, on exposure to air or on prolonged drying, became light blue. Analysis showed it to be a basic zinc salt having the formula



|         | Found. |       | Calculated. |
|---------|--------|-------|-------------|
|         | I.     | II.   |             |
| N ..... | 10·76  | —     | 10·96       |
| S ..... | 25·43  | 24·89 | 25·24       |

This zinc compound, when suspended in water and treated with hydrochloric acid until it lost its crystalline structure, became converted into the *dihydrochloride*. On dissolving the precipitate in water and adding excess of hydrochloric acid, the dihydrochloride separated in glistening leaflets, which were readily soluble in water, but nearly

insoluble in aqueous hydrochloric acid. On analysis, it gave the following numbers :

|          | Found. | Calculated for<br>$C_6H_2(NH_2)_2(SH)_2 \cdot 2HCl$ . |
|----------|--------|---|
| N ... .. | 11.45  | 11.43   |
| S ... .. | 26.16  | 26.12   |

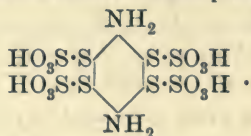
The *base* was readily obtained from the hydrochloride by adding sodium acetate to its hot aqueous solution, preferably in an atmosphere of carbon dioxide. The first precipitate, being somewhat dark, was removed ; the filtrate, on cooling, deposited large, colourless leaflets, which were washed with water and dried at  $100^\circ$ . The base, which was sparingly soluble in boiling water, melted at  $178-181^\circ$  with decomposition ; on exposure to air, it gradually became dark brown owing to oxidation.

Analysis gave numbers corresponding with the formula



|          | Found. | Calculated. |
|----------|--------|-------------|
| N ... .. | 16.21  | 16.27       |
| S ... .. | 36.45  | 37.20       |

*p-Phenylenediaminetetrathiosulphonic Acid,*



A solution of 54 grams of *p*-phenylenediamine in 440 grams of glacial acetic acid was mixed with 1200 grams of ice, and into this mixture, kept rapidly stirred, were then run simultaneously from two tap funnels in equal and tolerably rapid streams, solutions of 750 grams of sodium thiosulphate and of 283 grams of sodium bichromate, each in 1200 c.c. of water. From the resulting clear brown solution, potassium chloride precipitates the potassium tetrathiosulphonate as a crystalline substance having a bichromate-red colour. The product was collected, washed with aqueous potassium chloride, and digested with the same solution at its boiling point ; the yield was 63 grams. The salt, which now had the form of lemon-yellow needles, was recrystallised from water with the addition of animal charcoal. It then formed bright yellow needles rather less soluble than the potassium dithiosulphonate. The salt also crystallises in bright orange-red needles, which change very readily into the more stable yellow form.



The salt, when dried at  $100^{\circ}$ , gave the following numbers on analysis :

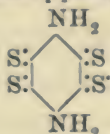
|         | Found. |       | Calculated for<br>$C_6(NH_2)_2/S \cdot SO_2K$ . |
|---------|--------|-------|---|
|         | I.     | II.   |   |
| C ..... | 10.37  | —     | 10.16   |
| H ..... | 0.62   | —     | 0.56  |
| N ..... | 3.70   | 4.00  | 3.95  |
| S ..... | 36.06  | 36.12 | 36.16   |
| K ..... | 21.87  | 22.04 | 22.03   |

The free tetrathiosulphonic acid is colourless and readily soluble in water. On treatment with nitrous acid, it is converted into a tetrazo-compound. This is a yellow, crystalline solid easily soluble in water, which, on the addition of sodium sulphide, gives a scarlet-red and then a violet-blue coloration.

A determination of the molecular weight of the potassium tetrathiosulphonate by titration with a standard solution of sodium nitrite gave the following result :

1.4456 grams of the salt required 41.4 c.c. *N*/10 nitrite for diazotisation. Molecular weight found = 698; calculated = 708.

*Tetrasulphido-p-phenylenediamine,*



On digesting a boiling solution of the potassium tetrathiosulphonate with concentrated hydrochloric acid, the solution became orange-coloured and evolved sulphur dioxide, while the hydrochloride of a new base gradually separated as a red, amorphous precipitate. As soon as the odour of sulphur dioxide had disappeared, the mixture was poured into water, which caused the decomposition of the red hydrochloride and the production of a deep black precipitate of the free base. This was collected, washed with water and dilute ammonia, and dried at  $160^{\circ}$ . The product forms a deep indigo-blue or black powder insoluble in all the usual solvents, but dissolving readily in aqueous sodium sulphide to a pale greenish-yellow solution.

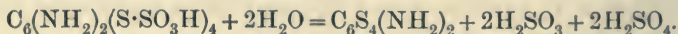
On analysis, it gave the following numbers :

|         | Found. | Calculated for<br>$C_6S_4(NH_2)_2$ |
|---------|--------|------------------------------------|
|         |        |                                    |
| C ..... | 30.98  | 31.03                              |
| H ..... | 1.90   | 1.72                               |
| N ..... | 11.75  | 12.06                              |
| S ..... | 53.8   | 55.20                              |

A determination of the quantity of sulphurous and sulphuric acid produced on boiling the tetrathiosulphonic acid with a mineral acid gave the following result :

|                               | Found. |       | Theory for<br>2 mol. proportions. |
|-------------------------------|--------|-------|-----------------------------------|
|                               | I.     | II.   |                                   |
| Sulphurous acid.....          | 21.01  | 21.65 | 23.15 per cent.                   |
| Sulphuric     ,,        ..... | 30.98  | —     | 27.68     ,,                      |

If the acid employed is sulphuric acid instead of hydrochloric acid, the proportion of sulphurous acid evolved is higher, being 22.23 per cent. On the other hand, if the decomposition is performed with hydrochloric acid at a higher temperature (200°) instead of at the boiling point, the quantity of sulphuric acid is increased to 33.08 per cent. It thus appears that a varying amount of the sulphurous acid is oxidised to sulphuric acid, but that the reaction takes place substantially according to the equation :



The yield of tetrasulphide base obtained also corresponds with this equation, being 33.93 per cent., whilst the theoretical yield is 32.76.

Attempts to prepare a tetrahydrosulphide from the tetrathiosulphonic acid by reduction with zinc dust gave an ochre-yellow, amorphous product which could not be purified.

*Dimethyl-p-phenylenediaminedithiosulphonic Acid,*  
 $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{NMe}_2)(\text{S}\cdot\text{SO}_3\text{H})_2.$

This acid, which was obtained by the same method as that already described for the unsubstituted dithiosulphonic acid, is, however, isolated with much more difficulty on account of its greater solubility, and the yield is therefore small. The potassium salt crystallises in yellow, transparent, rhombic plates ; the free acid, which is colourless, differs widely in its properties from the corresponding monothiosulphonic acid described by Bernthsen. Thus, instead of giving methylene blue when oxidised together with dimethylaniline, it produces a dark blue, bronzy precipitate which is insoluble in water or in aqueous acids or alkalis. Further, with nitrous acid, it gives a clear solution, and with a solution of sodium polysulphide an orange-red precipitate. Like the above-described di- and tetra-thiosulphonic acids of *p*-phenylenediamine, when oxidised together with a primary amine or diamine, it gives rise to black colouring matters which belong to the "Sulphide" class.

CXVIII.—*The Rotation of the Menthyl Esters of the Isomeric Chlorobenzoic Acids.*

By JULIUS B. COHEN and SAMUEL HENRY CLIFFORD BRIGGS.

IN the course of a research on the chlorination of toluene (Cohen and Dakin, *Trans.*, 1901, 79, 1111), the six isomeric dichlorobenzoic acids were obtained in a pure state by methods which, although tedious, gave without difficulty a satisfactory yield of each of the isomerides.

The rotation of the esters produced by condensing these acids with active alcohols seemed likely to throw some light on the effect of position isomerism on optical activity—a subject about which, from lack of data, our knowledge is at present very imperfect. We selected the esters of menthol as being most suitable for the purpose.

During the progress of the research, a paper by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 606) appeared giving the rotation of the three menthyl bromobenzoates. We have not been able to consult the original memoir, but the figures given in the abstract (*Abstr.*, 1903, ii, 1) accord in the main with those obtained by us from the corresponding monochloro-compounds and are referred to below.

In preparing the chlorobenzoic acids and the corresponding menthyl esters, the following general method was adopted. The acids, obtained from the chlorotoluenes by oxidation with dilute nitric acid in sealed tubes, were purified by recrystallisation from water or dilute alcohol and converted into the acid chlorides by the action of phosphorus pentachloride. The products of this reaction were separated by distillation under diminished pressure, the phosphorus oxychloride being removed by heating on the water-bath, whilst the acid chloride was obtained at higher temperatures. A mixture of the acid chloride and menthol in molecular proportion was heated in the oil-bath at about 130–140° until the evolution of hydrogen chloride ceased, when the product was made slightly alkaline with aqueous sodium carbonate and distilled in steam until all the unaltered menthol and menthyl chloride were removed. The ester was isolated from a chloroform extract of the acidified residue after dehydration over calcium chloride and removal of the solvent by distillation under diminished pressure. At the beginning of the distillation, a small quantity of solid, which proved to be the free acid, was observed in the distillate from some of the esters; but the decomposition was very slight and did not appear to affect the rotation of the clear liquid, which remained unchanged after being repeatedly redistilled.

The esters which showed signs of decomposition were those of the



*o*- and *p*-chlorobenzoic acids and the 2:3-, 2:5- and 3:4-dichlorobenzoic acids.

Evidence of steric hindrance is very clearly indicated in the case of the 2:6-dichlorobenzoic acid, for whereas the acid chlorides as a rule react vigorously with menthol at 135—140°, no reaction occurs with 2:6-dichlorobenzoyl chloride until the temperature reaches 180°, and even then it proceeds very slowly.

The following table gives the boiling points of the six dichlorobenzoyl chlorides.

| Dichlorobenzoyl chloride. | b. p. | Pressure in mm. | Dichlorobenzoyl chloride. | b. p.    | Pressure in mm. |
|---------------------------|-------|-----------------|---------------------------|----------|-----------------|
| 2·3                       | 140°  | 14              | 2·6                       | 142—143° | 21              |
| 2·4                       | 150   | 34              | 3·4                       | 159—160  | 42              |
| 2·5                       | 137   | 15              | 3·5                       | 135—137  | 25              |

The following table gives the boiling points, specific gravities, specific and molecular rotations of the series of menthyl esters, together with the corresponding constants for menthyl benzoate, which are included for the purpose of comparison.

| Ester.                               | Boiling or melting point.   | Pressure in mm. | Specific gravity 20°/4°.      | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|--------------------------------------|-----------------------------|-----------------|-------------------------------|---------------------------|----------------------|
| Menthyl <i>o</i> -chlorobenzoate ... | b. p. 225°                  | 30              | 1·0870                        | -66·24°                   | -195°                |
| „ <i>m</i> -chlorobenzoate...        | „ 218—219                   | 14              | 1·0822                        | -80·45                    | -236·9               |
| „ <i>p</i> -chlorobenzoate ...       | „ 231—232                   | 20              | 1·0804                        | -80·60                    | -237·3               |
| „ 2:3-dichlorobenzoate .....         | „ 229                       | 15              | 1·1607                        | -52·57                    | -172·9               |
| „ 2:4-dichlorobenzoate .....         | „ 218—219                   | 15              | 1·1546                        | -63·72                    | -209·6               |
| „ 2:5-dichlorobenzoate .....         | { „ 243—245<br>m.p. 28—29 } | { 35            | 1·1590                        | -60·62                    | -199·4               |
| „ 2:6-dichlorobenzoate .....         | „ 134—135                   | { not distilled | in CHCl <sub>3</sub> solution | -34·4                     | -113                 |
| „ 3:4-dichlorobenzoate .....         | b. p. 244—245               | 35              |                               |                           |                      |
| „ 3:5-dichlorobenzoate .....         | „ 223—225                   | 20              | 1·1535                        | -70·89                    | -233·2               |
| „ benzoate(Tschugaeff)               | m. p. 54                    | —               | { in benzene solution         | { -90·92                  | -236·3               |

The series of esters was analysed by estimating the quantity of chlorine present, with the following results :

*Analyses of the Chlorobenzoic Esters.*

| Ester.                         | Substance taken. | AgCl found. | Percentage of chlorine. |             |
|--------------------------------|------------------|-------------|-------------------------|-------------|
|                                |                  |             | Found.                  | Calculated. |
| Menthyl o-chlorobenzoate ..... | 0.2530           | 0.1235      | 12.06                   | 12.04       |
| „ m-chlorobenzoate .....       | 0.2502           | 0.1234      | 12.14                   | „           |
| „ p-chlorobenzoate .....       | 0.2717           | 0.1317      | 11.98                   | „           |
| „ 2:3-dichlorobenzoate.....    | 0.2938           | 0.2587      | 21.76                   | 21.56       |
| „ 2:4-dichlorobenzoate.....    | 0.2793           | 0.2423      | 21.44                   | „           |
| „ 2:5-dichlorobenzoate.....    | 0.2744           | 0.2375      | 21.40                   | „           |
| „ 2:6-dichlorobenzoate.....    | 0.2550           | 0.2235      | 21.67                   | „           |
| „ 3:4-dichlorobenzoate.....    | 0.2921           | 0.2490      | 21.08                   | „           |
| „ 3:5-dichlorobenzoate.....    | 0.2489           | 0.2185      | 21.70                   | „           |

On reference to the properties of the isomeric dichlorobenzoic esters, it will be seen that the 2:6-compound is distinguished from the other isomerides by its high melting point; this substance is, nevertheless, monomolecular as indicated by a molecular weight determination by the cryoscopic method in benzene.

| $\alpha$ | W    | $\Delta t$ | M.   |
|----------|------|------------|------|
| 0.1031   | 10.3 | 0.151°     | 331  |
| 0.1016   | „    | 0.163      | 303  |
| 0.1113   | „    | 0.169      | 319. |

Mean of 3 experiments,  $M = 318$ ; Cal.,  $C_{17}H_{22}O_2Cl_2$  requires  $M = 329$ .

Owing to the high melting point, we were unfortunately unable to determine the rotation of the melted substance; moreover, it is so slightly soluble in all solvents that it was impossible to obtain strong solutions, and thus calculate the rotation of the pure substance by extrapolation. We had to be satisfied with finding the rotation in a chloroform solution containing 6.36 per cent. of the substance, which gave a specific rotation of  $[\alpha]_D^{20} = -34.4^\circ$ , which may be regarded as an approximation. It seems reasonable to conclude, however, that the rotation would be low, and probably much lower than that of any of the other compounds of the series.

The order of magnitude, beginning with the ester of lowest rotation, is as follows:

2:6, 2:3, ortho, 2:5, 2:4, 3:4, 3:5, phenyl, meta, para.

Three conclusions may be drawn from the above experimental data.

(1) The greatest effect in decreasing the rotation of the unsubstituted menthyl ester is produced when the halogen enters the ortho-position

with respect to the ester radicle; the least alteration is observed when the halogen is in the meta- or para-position, the introduction of a single halogen atom in the latter position slightly increasing the rotation. (2) The monohalogen esters accord with the rule laid down by Frankland and Wharton (Trans., 1896, 69, 1320, 1583), and confirmed by Guye and Babel (Abstr., 1899, 76, ii, 719) and by Tschugaeff (Abstr., 1903, 84, ii, 2), and follow the order:—ortho, phenyl, meta, para. (3) Two halogens attached to adjacent carbon atoms of the nucleus (2:3 and 3:4) produce a greater effect than either halogen singly.

The results obtained with the monochlorobenzoic esters show a general correspondence with the monobromobenzoic esters examined by Tschugaeff (*loc. cit.*).

| Tschugaeff.             | $[M]_D^{20^\circ}$ . | C. and B.                | $[M]_D^{20^\circ}$ . |
|-------------------------|----------------------|--------------------------|----------------------|
| Menthyl benzoate .....  | -236.3°              | Menthyl benzoate .....   | -236.3°              |
| „ o-bromobenzoate ..... | -205.3               | „ o-chlorobenzoate ..... | -195.0               |
| „ m-bromobenzoate ..... | -238.7               | „ m-chlorobenzoate ..... | -236.9               |
| „ p-bromobenzoate ..... | -238.8               | „ p-chlorobenzoate ..... | -237.3               |

When compared with the rotation of the ortho-chloro-ester, the number for the ortho-bromo-ester seemed too high. We therefore repeated the preparation of this compound, and obtained a slightly lower result, namely,  $[M]_D^{20^\circ} = -201.0^\circ$ , but this is still much higher than the constant for the chlorine compound.

In regard to the dichlorobenzoic esters, it is of interest to notice the rotations of the 2:3- and 2:5-esters. In both compounds, the chlorine atoms occupy the ortho- and meta-positions, yet they show a wide difference in rotation. Instead of the rotations being approximately the same and lying between those of the ortho- and meta-compounds, the constant for the 2:3-compound is much lower, and that of the 2:5-compound is slightly higher, than the value obtained for the ortho-compound. The difference might be attributed to the variation in the position of the centre of gravity of the masses in the two cases according to the theory of Guye, but the low rotation of the 3:4- and 3:5-isomerides is directly opposed to the principle of the lever-arm (Frankland and Wharton, *loc. cit.*).

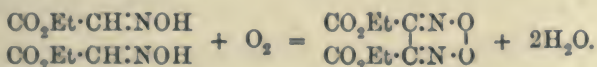
A careful examination of the results obtained by different observers on the effect of position isomerism on optical activity leads to the conclusion that a satisfactory generalisation based on existing data has yet to be found.



CXIX.—*The Action of Nitric Acid on Methyl Dimethylacetoacetate.\**

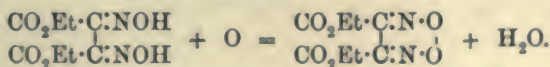
By W. H. PERKIN, Ph.D., F.R.S.

THE first experiments on the action of nitric acid on ethyl acetoacetate appear to have been carried out in 1883 by Pröpper (*Annalen*, 1884, 222, 48), who obtained, as the product of the action, an oil, which he named "oximinoacetic ester," and to which he gave the formula  $C_4H_7O_3N$ . In the year 1890, Crämer (*Ber.*, 23, 3496) succeeded in preparing oximinoacetic acid in a pure state from glyoxylic acid by the action of hydroxylamine,  $CHO \cdot CO_2H + NH_2OH = CH(:NOH) \cdot CO_2H$ , and showed that the ethyl ester derived from this acid was not identical with Pröpper's compound. When, however, ethyl oximinoacetate is treated with nitric acid, it is readily oxidised with formation of ethyl glyoximeperoxidedicarboxylate:

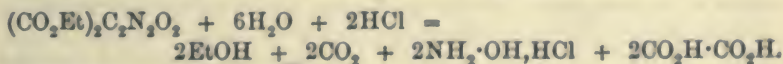


Crämer conclusively proved that it is the latter ester which is the substance formed when ethyl acetoacetate is treated with nitric acid under the conditions employed by Pröpper.†

That the ester obtained by these two different methods has the constitution given to it by Crämer was subsequently confirmed by Walter Beckh (*Ber.*, 1897, 30, 152), who obtained the same ester from ethyl dioximinosuccinate by treatment with nitric acid:



In view of the results to be described in the present paper, it is interesting to notice that ethyl glyoximeperoxidedicarboxylate is readily decomposed by strong acids or alkalis; thus, caustic soda hydrolyses it with formation of carbon dioxide, alcohol, hydrocyanic and oxalic acids, whereas on boiling with hydrochloric acid it is converted into carbon dioxide, alcohol, hydroxylamine, and oxalic acid, the latter decomposition being represented by Crämer thus:



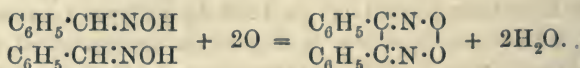
Although few examples have, so far, been worked out in detail, it

\* A short account of this research has already appeared in the Proceedings, 1901, 17, 204.

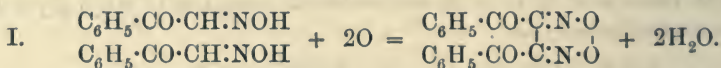
† Compare also L. Bouveault (*Compt. rend.*, 1901, 132, 1569, and *Bull. Soc. chim.*, 1902, [iii], 27, 1160).

seems probable that the formation of glyoximeperoxide derivatives by the action of nitric acid and other oxidising agents on oximes is a reaction of wide applicability. This reaction has, for example, been observed in the case of certain aromatic oximes.

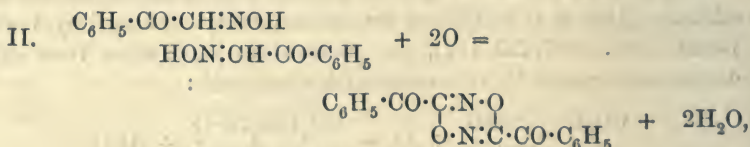
Thus, benzaldoxime, when oxidised by nitrogen peroxide or potassium ferricyanide, yields diphenylglyoximeperoxide,



A case much more closely related to the subject matter of this paper, and which therefore requires fuller discussion, has been described by Holleman (*Ber.*, 1888, 21, 2835), who showed that nitrosoacetophenone, when acted on by concentrated nitric acid, is converted into diphenyldinitrosacyl (dibenzoylglyoximeperoxide)\*:

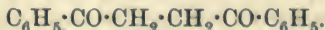


It must, however, be pointed out that the oxidation of oximes in general, and of nitrosoacetophenone in particular, does not necessarily lead to the formation of a derivative of glyoximeperoxide. The removal of the four atoms of hydrogen might also take place according to the following scheme:



a possibility which, so far, seems to have escaped notice.

That diphenyldinitrosacyl is dibenzoylglyoximeperoxide is, however, proved by the observation of Holleman that, on reduction with zinc dust and acetic acid, it yields dibenzoylthane,

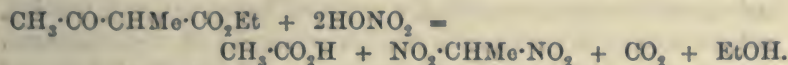


\* Compare also the formation of dimethylglyoximeperoxide,  $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{N}\cdot\text{O} \\ \text{Me}\cdot\text{C}\cdot\text{N}\cdot\text{O} \end{array}$ , by the action of nitrogen peroxide on dimethylglyoxime,  $\text{Me}\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{Me}$ , as also the formation of methylethylglyoximeperoxide under similar conditions (Scholl, *Ber.*, 1890, 23, 3498). A good account of some of the more important researches on derivatives of glyoximeperoxide is to be found in Roscoe-Schorlemmer, *Lehrbuch der Chemie* (Vol. V. p. 1268, published in 1899). The name "glyoximeperoxide" is retained in this research because it has been adopted, not only in the foregoing manual (*loc. cit.*), but also in Beilstein's *Handbuch* and other well-known books.

It is, however, obviously not a correct expression for the grouping  $\begin{array}{c} \text{CH}\cdot\text{N}\cdot\text{O} \\ \text{CH}\cdot\text{N}\cdot\text{O} \end{array}$ .

In this connection, it is interesting to note that when nitric acid acts on nitrosoacetophenone, a second substance is formed, which is isomeric with diphenylnitrosacyl and possesses quite different properties. It seems probable that this second substance may have been formed by the process represented in equation II.

When monoalkyl-substitution products of ethyl acetoacetate are treated with strong nitric acid, the reaction proceeds in quite a different direction to that observed by Pröpper in the case of ethyl acetoacetate itself. Thus, ethyl methylacetoacetate is converted into dinitroethane by nitric acid,

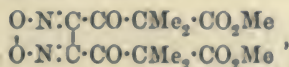


Ethyl ethylacetoacetate, under similar conditions, yields dinitropropane,  $\text{Et} \cdot \text{CH}(\text{NO}_2)_2$  (Chancel, *Jahresbericht*, 1883, 1079).

While I was engaged in preparing dinitroethane and dinitropropane by this method of Chancel's, it occurred to me to see what would happen if a disubstitution product of ethyl acetoacetate were treated with strong nitric acid, and the experiment which was then tried with methyl dimethylacetoacetate was the starting point in the present research.

When methyl dimethylacetoacetate,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Me}$ , is warmed with concentrated nitric acid, it is oxidised with formation of dimethylmalonic acid and a beautifully crystalline substance (m. p.  $65^\circ$ ) having the composition  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .

The properties of this new substance so closely resemble those of Holleman's diphenyldinitrosacyl and other similar glyoximeperoxide derivatives that there can scarcely be a doubt that its constitution must be represented by the formula



and I therefore propose to name it *methyl glyoximeperoxide tetramethyl dimalonylate*, but, for the sake of brevity, it will often be referred to in this introduction and in the experimental part of this paper as the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .

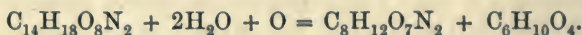
The investigation of this substance has led to the preparation of a large number of derivatives and the examination of these has made it possible, in most cases, to assign to them constitutional formulæ which are thought to be satisfactory. In some of the decompositions studied, however, the reactions taking place are so complex, and the compositions of the resulting compounds so remarkable, that it has only been possible to suggest constitutional formulæ, and, until further data are available, these are to be considered only as approximations. Under



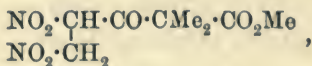
these circumstances, it will economise space as well as facilitate the understanding of the results if the principal facts are grouped together and discussed in an introduction before the experimental details are described.

When the substance  $C_{14}H_{18}O_8N_2$  is boiled with caustic potash, it is completely decomposed with the formation of methyl alcohol, ammonia, carbon dioxide, hydrocyanic acid, isobutyric acid, and dimethylmalonic acid, the decomposition being similar to that which Pröpper observed to take place in the case of ethyl glyoximeperoxidedicarboxylate (p. 1217). If, however, it is treated with sodium ethoxide in the cold and the solution at once acidified, a profound decomposition is avoided, and the product of the reaction consists principally of two substances, namely, methyl hydrogen dimethylmalonate,  $CO_2Me \cdot CMe_2 \cdot CO_2H$ , and a crystalline substance melting at  $145^\circ$  which has the formula  $C_8H_{12}O_7N_2$ . The latter substance has acid properties, contains one methoxyl group, and, when treated with phenylhydrazine, yields a compound having the formula  $C_{14}H_{16}O_4N_4$  which is identical with that obtained by the direct action of phenylhydrazine on the substance  $C_{14}H_{18}O_8N_2$  (p. 1224).

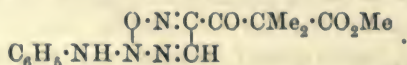
It is very difficult to understand the formation of the substance  $C_8H_{12}O_7N_2$  from  $C_{14}H_{18}O_8N_2$  by the action of sodium ethoxide in the cold, but, if the fact is taken into account that the remaining six carbon atoms have been removed in the form of methyl hydrogen dimethylmalonate,  $(C_6H_{10}O_4)$ , it is obvious that simultaneous hydrolysis and oxidation must have taken place according to the equation:



A careful consideration of the properties of the substance  $C_8H_{12}O_7N_2$  makes it appear probable that it has the constitution represented by the formula



and it has therefore, provisionally, been named *methyl  $\alpha\beta$ -dinitroethane-dimethylmalonylate*. Although it does not contain a carboxyl group, a substance of this constitution would nevertheless possess acid properties, because it is a derivative of a dinitroparaffin, and nitroparaffins exhibit acid properties. Moreover, if this constitution is accepted, then it becomes easy to understand how such a substance, when treated with phenylhydrazine (p. 1238), yields the compound  $C_{14}H_{16}O_4N_4$ , which, it can scarcely be doubted, has the constitution

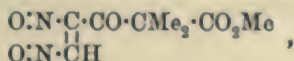


The compound  $C_8H_{12}N_2O_7$  undergoes a very extraordinary decom-

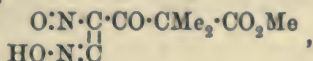
position when simply recrystallised from a mixture of ether and toluene, whereby it is converted into a new and well-defined colourless substance having the formula  $C_8H_{10}O_5N_2$  (m. p.  $169^\circ$ ).

Apparently self-oxidation, due to the presence of the two nitro-groups, takes place, and this change may be assumed to proceed according to the equation:  $C_8H_{12}O_7N_2 = C_8H_{10}O_5N_2 + H_2O + O$ .

It is therefore suggested that the constitution of the substance  $C_8H_{10}O_5N_2$  may be represented either by the formula



or, perhaps more probably, by the tautomeric (oxime) modification of this formula, that is,

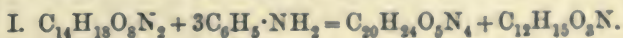


since the substance  $C_8H_{10}O_5N_2$  is capable of neutralising exactly one molecular proportion of NaOH. It has therefore been named, provisionally, *methyl  $\alpha\beta$ -dinitrosoethylenedimethylmalonylate*.

It will be seen from the above that the action of cold sodium ethoxide on the substance  $C_{14}H_{18}O_8N_2$  proceeds in a very remarkable way, and for this reason it is proposed to investigate the behaviour of some more simply constituted glyoximeperoxide derivatives with alkalis, in order, if possible, to obtain further clues to the course of the reaction.

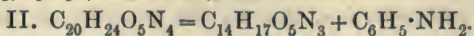
*Action of Ammonia, of Aniline, and of p-Chlorotuniline on the Substance*  
 $C_{14}H_{18}O_8N_2$

When the substance  $C_{14}H_{18}O_8N_2$  is treated with strong aqueous ammonia, vigorous action sets in, and the only product which could be isolated was *dimethylmalonamide*,  $NH_2 \cdot CO \cdot CMe_2 \cdot CO \cdot NH_2$  (m. p.  $263^\circ$ ). If, however, the reaction is moderated by diluting with ether, *methyl dimethylmalonamate*,  $CO_2Me \cdot CMe_2 \cdot CO \cdot NH_2$  (m. p.  $86^\circ$ ), is produced, together with another compound which is not easily isolated. The examination of the latter substance, although doubtless of great interest, was not pursued, because it was found that the products obtained by substituting aniline for ammonia were very much better characterised, and therefore better suited for detailed investigation. If the compound  $C_{14}H_{18}O_8N_2$  is treated with aniline under the conditions described in detail in the experimental part, it yields a sparingly soluble substance,  $C_{20}H_{24}O_5N_4$  (m. p.  $110^\circ$ ), and a more readily soluble product,  $C_{12}H_{15}O_3N$  (m. p.  $80^\circ$ ), according to the equation:

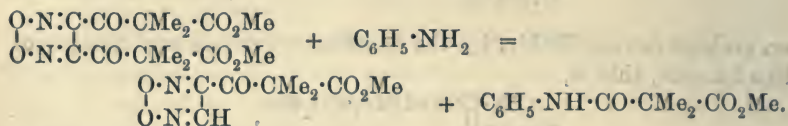




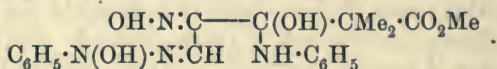
The substance  $C_{20}H_{24}O_5N_4$ , when dissolved in cold hydrochloric acid, decomposes into aniline hydrochloride and a substance having the formula  $C_{14}H_{17}O_5N_3$  (m. p.  $140^\circ$ ), thus:



The explanation of these decompositions is probably as follows: In the first place, the substance  $C_{14}H_{18}O_8N_2$  is decomposed by aniline with the elimination of one of the methyl dimethylmalonyl groups  $-CO \cdot CMe_2 \cdot CO_2Me$ , this complex then combining with aniline to form *methyl dimethylmalonanilate* (that is, the substance  $C_{12}H_{15}O_3N$  shown in equation I):



The intermediate glyoximeperoxide derivative then at once reacts with the excess of aniline present to form the substance  $C_{20}H_{24}O_5N_4$ . This change is not confined to the glyoximeperoxide portion of the molecule, because aniline also becomes added to the carbonyl group of the methyl dimethylmalonyl residue, and the constitution of the substance  $C_{20}H_{24}O_5N_4$  may therefore be represented by the formula

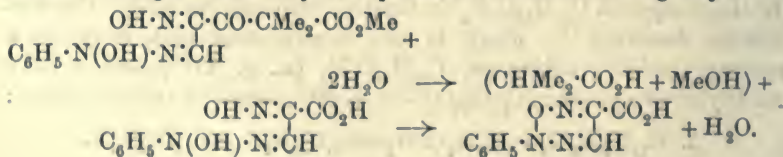


This substance, to which the name *methyl dianilinoglyoximedimethylmalonylate* is given, when treated with hydrochloric acid, loses the aniline residue which is loosely bound to the carbonyl group, and the product  $C_{14}H_{17}O_5N_3$  is therefore *methyl anilinoglyoximedimethylmalonylate* having the following constitution:



Its properties are in accordance with this formula; it forms salts because of its substituted phenylhydroxylamine group  $C_6H_5 \cdot N(OH)$ , and is also acidic, dissolving in aqueous alkalis because of the presence of the oxime group  $OH \cdot N : C <$ .

A very striking property of the substance  $C_{14}H_{17}O_5N_3$  is that under certain conditions it is decomposed by caustic soda into isobutyric acid and a brilliant red acid having the formula  $C_9H_7O_3N_3$ , a series of changes which may be represented in the following way:





This interesting acid, which has been named *phenylisotriazoxole-carboxylic acid*,\* melts at  $155^{\circ}$  and decomposes, on further heating, with slight explosion; it yields a bright red, crystalline silver salt,  $C_9H_5O_3N_3Ag$ . The change from the colourless anilino-glyoxime derivative to the intensely red isotriazoxole derivative, a change of colour due to the closing of the isotriazoxole ring, is most interesting.

Owing to the complicated nature of the reactions explained above, it was thought advisable to confirm the composition of the products of the action of aniline on the substance  $C_{14}H_{18}O_8N_2$  by carrying out a second series of experiments in which *p*-chloroaniline was employed in the place of aniline. The determination of chlorine in the compounds thus obtained would then serve as a further means of checking their molecular weights and indirectly the molecular weights of the compounds obtained with the aid of aniline itself. The actual results of the experiments with *p*-chloroaniline fully confirmed those which had been obtained with aniline, and they may therefore be quite briefly summarised as follows.

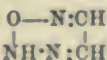
The substance  $C_{14}H_{18}O_8N_2$  reacts with *p*-chloroaniline to form *methyl di-p-chloroanilinoglyoximedimethylmalonylate* (p. 1246) and *methyl dimethylmalon-p-chloroanilate* (p. 1247).

I.  $C_{14}H_{18}O_8N_2 + 3C_6H_4Cl \cdot NH_2 = C_{20}H_{22}O_5N_4Cl_2 + C_{12}H_{14}O_3NCl$ ; the former substance is converted, by the action of hydrochloric acid, into *p*-chloroaniline hydrochloride and *methyl p-chloroanilinoglyoxime-dimethylmalonylate* (p. 1246).

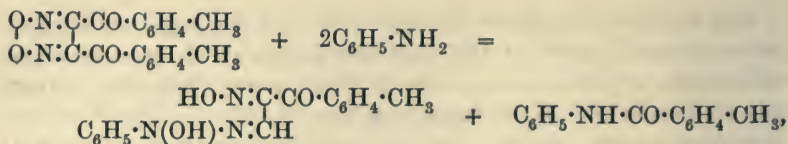
II.  $C_{20}H_{22}O_5N_4Cl_2 = C_{14}H_{18}O_8N_2Cl + C_6H_4Cl \cdot NH_2$ .

Lastly, the substance  $C_{14}H_{18}O_8N_2Cl$ , when treated with caustic soda, yields a red, crystalline acid which is obviously *p-chlorophenylisotriazoxolecarboxylic acid*,  $C_9H_5O_3N_3Cl$ .

In giving the above explanation of the mechanism of the action of aniline on the substance  $C_{14}H_{18}O_8N_2$ , attention should be called to the fact that several decompositions of a similar nature have already been investigated, and, as an illustration, it will suffice to give the following example, which has a direct bearing on the case in point. In the course of his important researches on derivatives of glyoxime-peroxide (*loc. cit.*, see footnote, below), Boeseken treated di-*p*-toluoyl-glyoximeperoxide with aniline, and showed that the reaction takes place in the following way:

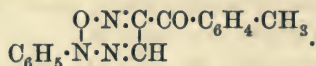


\* The ring  $\begin{array}{c} O-N:CH \\ | \\ NH:N:CH \end{array}$  has been named "*isotriazoxol*" by Boeseken (*Rec. trav. chim.*, 1897, 16, 297—353; *Abstr.*, 1898, i, 496), but in the new edition of Roscoe and Schorlemmer's *Lehrbuch der Chemie* (Vol V., p. 1278) it is named "*isoxox-diazin*." In this paper I have adopted the former,



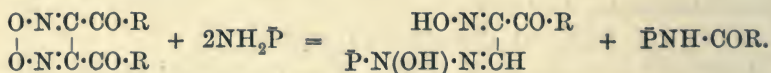
and it is obvious that this decomposition corresponds very closely with that which takes place when the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  is treated with aniline.

The intermediate substance obtained by Boeseken, and figured above, readily loses water on heating with the formation of the deep red *p*-toluoylphenylisotriazoxole,



The elimination of water could not be directly brought about in the case of methyl anilino-glyoximidemethylmalonylate, because this substance decomposes on heating. The closing of the ring was, however, ultimately accomplished with the aid of caustic soda, when phenylisotriazoxolecarboxylic acid was obtained, as explained on pp. 1223 and 1248.

The action of primary amino-compounds, and other primary amines, on derivatives of glyoximeperoxide containing two acidic side-chains appears to be a general one, and to take place according to the following scheme :



The condensation product containing two hydroxyl groups may sometimes be isolated, but it is frequently not sufficiently stable, water being spontaneously eliminated with the formation of the isotriazoxole derivative. It is remarkable that, in all the cases so far investigated, only one of the acid radicles is removed by the action of the amino-compound, and this is even the case when both the radicles are not only of the same nature, but are also exactly similarly situated.

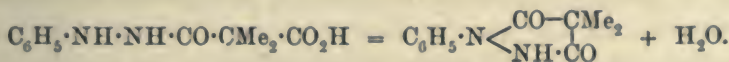
*The Action of Phenylhydrazine, of p-Bromophenylhydrazine, and of Semicarbazide on the Substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .*

When treated with phenylhydrazine under the conditions stated in the experimental part of this paper (p. 1249), the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  yields a colourless, crystalline compound,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$  (m. p.  $111^\circ$ ), and a bright red, crystalline derivative,  $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$  (m. p.  $154^\circ$ ). If *p*-bromophenylhydrazine is employed in the place of phenylhydrazine, an exactly similar reaction takes place, resulting in the formation of

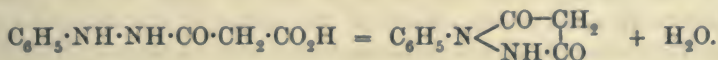


a colourless substance,  $C_{12}H_{16}O_3N_2Br$  (m. p.  $96^\circ$ ), and an orange-coloured substance,  $C_{14}H_{15}O_4N_4Br$  (m. p.  $159^\circ$ ). In discussing the constitution of these products, the derivatives obtained with the aid of phenylhydrazine may be taken as the example.

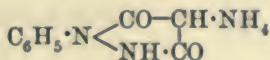
The substance  $C_{12}H_{16}O_3N_2$  is *methyl phenylhydrazidimethylmalonate*,  $CO_2Me \cdot CMe_2 \cdot CO \cdot NH \cdot NH \cdot C_6H_5$ . When warmed with caustic potash, it dissolves, and, on acidifying, a new compound separates which melts at  $177^\circ$  and has the formula  $C_{11}H_{12}O_3N_2$ . In the formation of this substance according to the equation  $C_{12}H_{16}O_3N_2 + H_2O = C_{11}H_{12}O_3N_2 + H_2O + MeOH$ , hydrolysis first takes place, and the resulting phenylhydrazidimethylmalonic acid then undergoes spontaneous condensation with loss of water and formation of 1-phenyl-4:4-dimethyl-3:5-pyrazolidone,



This behaviour is exactly similar to that of ethyl phenylhydrazidimalonate, which dissolves in caustic potash and, on acidifying, yields 1-phenyl-3:5-pyrazolidone (Burmeister and Michaelis, *Ber.*, 1891, 24, 1801; 1892, 25, 1506):

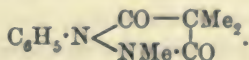


The latter substance dissolves readily in alkalis and even in dilute ammonia, and Burmeister and Michaelis take it for granted that the acid properties of the substance are due to a hydrogen atom of the  $CH_2$  radicle being acidic, doubtless on account of its proximity to the two CO groups. They therefore write the formula of the crystalline ammonium salt as follows:



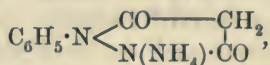
(*loc. cit.*, p. 1508).

The phenyldimethylpyrazolidone obtained from methyl phenylhydrazidimethylmalonate in the way described above has, however, most pronounced acid properties in spite of the fact that both the hydrogen atoms of the  $CH_2$  group are already substituted (by methyl); it even dissolves in aqueous sodium carbonate and, when heated with alcoholic caustic soda and methyl iodide, is readily converted into 1-phenyl-2:4:4-trimethyl-3:5-pyrazolidone (m. p.  $72^\circ$ ), which, since it does not contain a methoxyl group, can only have the formula



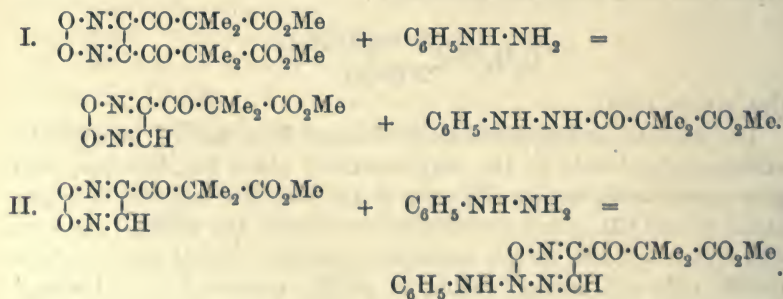


Arguing from these results, it seems probable that the acidity of 1-phenyl-3:5-pyrazolidone is due to the hydrogen of the NH group and not to one of the hydrogen atoms of the CH<sub>2</sub> group, and therefore the constitution of its ammonium salt is probably that represented by the formula



and is not that figured on p. 1225. An examination of the formula of phenylpyrazolidone shows at once that only one of the CO groups attached to the CH<sub>2</sub> group is ketonic, and therefore, although the latter group may be capable of condensing with aldehydes (as Burmeister and Michaelis show is the case), it can hardly be expected that its hydrogen atoms would be sufficiently acidic to react with alkali carbonates. If it be true that the acidic nature of phenylpyrazolidone is entirely due to the NH group, this fact will necessitate an alteration in such formulæ of the derivatives of this substance as have been constructed on the assumption that the acidity is due to the CH<sub>2</sub> group. In any case, the very strong acid nature of phenylpyrazolidone, and especially of the phenyldimethylpyrazolidone described above, is very remarkable.

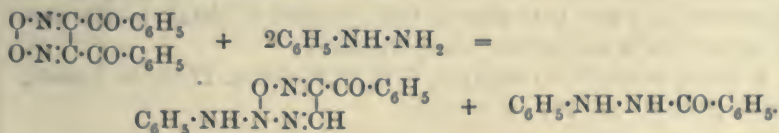
Returning again to the question of the nature of the change which takes place when phenylhydrazine reacts with the substance C<sub>14</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub>, there can be little doubt, from the examination of the substance C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub> and from the fact that one of the products of the reaction is methyl phenylhydrazidimethylmalonate, that the phenylhydrazine attacks the glyoximeperoxide ring in a precisely similar manner to that already described in the case of the action of aniline (p. 1221). In other words, the change may be represented thus:



The substance C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub> has therefore been named *methylphenyl-aminoisotriazoxoledimethylmalonylate*. As a confirmation of this view of the constitution of this substance may be mentioned the fact that it crystallises in deep red crystals, and one of the most striking

characteristics of isotriazoxole derivatives is their intense red or reddish-brown colour. It is, nevertheless, remarkable that, in the formation of the compound  $C_{14}H_{16}O_4N_4$ , the phenylhydrazine should exclusively attack the glyoximeperoxide portion of the molecule and should show no tendency to react with either of the two carbonyl groups in the substance  $C_{14}H_{18}O_8N_2$ . It may, however, be mentioned that, especially in the camphor group, cases have been observed in which substances containing the grouping  $-CO \cdot CMe_2-$  (that is, a CO group next to a tertiary carbon atom) exhibit a remarkable inactivity towards phenylhydrazine.

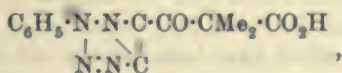
An analogous case to the above has also been investigated by Boeseken (*loc. cit.*), who showed that dibenzoylglyoximeperoxide reacts with phenylhydrazine with formation of phenylaminobenzoyliso-triazoxole in the following manner:



In this case, also, the phenylhydrazine showed no tendency to react with the two carbonyl groups contained in the dibenzoylglyoximeperoxide.

The red substance  $C_{14}H_{16}O_4N_4$  dissolves in caustic soda, and a yellow, crystalline sodium salt subsequently separates; this, on acidifying, yields an acid which melts at  $164^\circ$  and has the composition  $C_{13}H_{12}O_3N_4$ . This curious formula is confirmed by the fact that the red compound  $C_{14}H_{18}O_4N_4Br$ , obtained by the action of *p*-bromophenylhydrazine on the substance  $C_{14}H_{18}O_8N_2$ , behaves in a similar manner, yielding an acid having the corresponding formula,  $C_{13}H_{11}O_3N_4Br$ , on treatment with caustic soda (see pp. 1253).

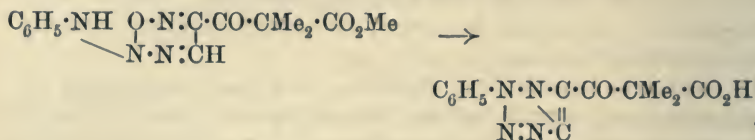
The acid  $C_{13}H_{12}O_3N_4$  crystallises in buff scales and is monobasic, as is shown by titration and by the analyses of the sparingly soluble calcium and barium salts,  $(C_{13}H_{11}O_3N_4)_2Ca$  and  $(C_{13}H_{11}O_3N_4)_2Ba$ . The almost colourless *methyl ester*, prepared from the sodium salt by heating with methyl iodide, melts at  $89^\circ$  and has the formula  $C_{13}H_{11}(Me)O_3N_4$ . It has been found very difficult to construct a satisfactory formula for this remarkable acid owing to the very small proportion of hydrogen which it contains, but it is thought that the configuration



is probably correct, and the name suggested, provisionally, for the acid is *phenyltetrazinedimethylmalonylic acid*.

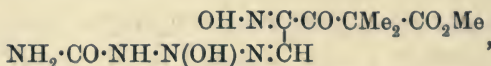
The mechanism of the formation of this acid from the substance  $C_{14}H_{16}O_4N_4$  is supposed to be as follows.

Hydrolysis of the ester takes place, and the hydrogen atom of the NH group, together with that of the CH group indicated in the following formula, combine with the oxygen atom of the isotriazoxole ring to form water, and then, by a necessary rearrangement of valencies, the formula proposed for the acid  $C_{13}H_{12}O_3N_4$  is obtained :



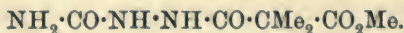
*Semicarbazide* reacts readily with the substance  $C_{14}H_{18}O_8N_2$ , and apparently in a way analogous to that discussed in detail in the case of the actions of aniline and phenylhydrazine.

A white, crystalline substance,  $C_9H_{15}O_6N_5$  (m. p.  $170^\circ$ ), is formed, which probably has the constitution



and this has been named *methyl semicarbaziglyoximedimethylmalonylate*. The fact that this substance is colourless shows that it cannot be an isotriazoxole derivative, but it is interesting to note that at its melting point it is converted, with evolution of gas, into a reddish-brown substance, which is probably the corresponding isotriazoxole derivative produced by the elimination of water between the two hydroxyl groups in the above formula.

The mother liquors from the substance  $C_9H_{15}O_6N_5$  contain a second compound which has not been examined, but which, judging from analogy, is probably methyl semicarbazidimethylmalonylate,



*The Behaviour of the Substance  $C_{14}H_{18}O_8N_2$  on Treatment with Reducing Agents.*

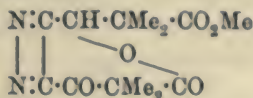
The action of reducing agents on the substance  $C_{14}H_{18}O_8N_2$  is a very vigorous one, and leads to the formation of a variety of new substances, several of which have been isolated and examined.

In the first experiments, the reducing agent employed was tin and hydrochloric acid, and from the product of the reduction three substances were isolated, namely :



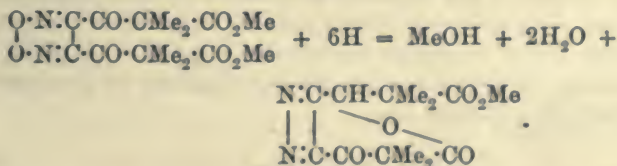
- (A) A substance having the formula  $C_{13}H_{16}O_5N_2$  (m. p.  $177^\circ$ ).  
 (B) " " "  $C_{14}H_{20}O_5N_2$  (m. p.  $154^\circ$ ).  
 (C) " " "  $C_{14}H_{20}O_5N_2$  (m. p.  $177^\circ$ ).

The substance (A) is probably the lactone of the *methyl ester* of *glyoxinedihydroxytetramethyldimalonylic acid*, and has the constitution represented by the formula



In experimenting with the view of determining the constitution of this substance, it was found, by means of Zeisel's method, that one methoxyl group was present, and it was therefore concluded that the substance is a methyl ester. Furthermore, as acetyl chloride is without action, it evidently does not contain any free hydroxyl groups. When boiled in alcoholic solution with semicarbazide hydrochloride and sodium acetate, it yields a *semicarbazone*,  $C_{14}H_{18}O_5N_3$ , and treatment with hydroxylamine results in the formation of the *oxime*,  $C_{13}H_{17}O_5N_2$ ; phenylhydrazine and *p*-bromophenylhydrazine lead also to condensation products, which, however, have not been analysed.\* These experiments, therefore, indicate that the substance  $C_{13}H_{16}O_5N_2$  contains a carbonyl group. When this substance is boiled with alcoholic potash, it undergoes profound decomposition with formation of ammonia, methyl alcohol, and hydrocyanic, *isobutyric*, and dimethylmalonic acids. At the ordinary temperature, the alkali simply hydrolyses the methyl ester with formation of the free lactonic acid, a crystalline substance which melts at  $214^\circ$ .

These properties all indicate that the constitution of the substance (A) should be the one represented above; in its formation from the substance  $C_{14}H_{18}O_5N_2$ , the glyoximeperoxide ring has undergone deoxidation, one of the carbonyl groups has been reduced, and lactone formation has also taken place:

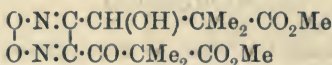


The latter formula is that of an  $\epsilon$ -lactone. Since, however, Baeyer and Villiger (*Ber.*, 1897, 30, 1954) have shown that dimethylmalic

\* It is remarkable that these reagents should condense more readily with the ketone group in this substance than with the two similar groups in the substance  $C_{14}H_{18}O_5N_2$  (p. 1219).

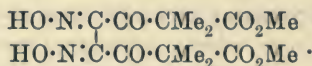
acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , readily yields a  $\beta$ -lactone, it is possible that the substance  $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_2$  may be a  $\beta$ -lactone because, if it is assumed that one of the dimethylmalonyl residues in the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  is converted into  $-\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  during reduction, the same grouping is produced as is present in dimethylmalic acid.

The substance (B) having the formula  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  and melting point  $154^\circ$  is probably *methyl glyoximeperoxidetetramethyldimalonylate*, and has the constitution

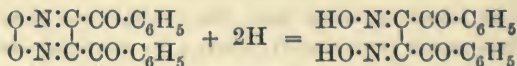


It yields a *semicarbazone*,  $\text{C}_{15}\text{H}_{23}\text{O}_8\text{N}_5$ , and, as will be seen from its formula, it represents the simplest product of the reduction of the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .

The substance (C), also having the formula  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  but melting at  $177^\circ$ , has been named *methyl glyoximetetramethyldimalonylate*, and its constitution is probably that represented by the formula

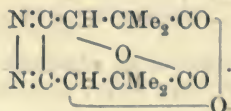


That it contains two hydroxyl groups is shown by the fact that, when boiled with acetic anhydride, it yields a diacetyl compound,  $\text{C}_{14}\text{H}_{18}\text{N}_2(\text{C}_2\text{H}_3\text{O})_2\text{O}_8$ . The formation of the corresponding dioxime from glyoximeperoxide derivatives by reduction appears to be a general property of the latter. Thus dibenzoylglyoximeperoxide, on careful reduction with zinc dust and acetic acid, yields dibenzoylglyoxime,



(Angeli, *Ber.*, 1893, 26, 527).

When the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  is treated with zinc dust and acetic acid, the course of the reaction is different to that described above in the case of tin and hydrochloric acid. The principal product obtained is a pale yellow substance having the formula  $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$ , which melts at about  $275^\circ$  and is evidently the *dilactone* of *glyazine-tetrahydrotetramethyldimalonylic acid*,



This same substance is also produced when any of the three compounds, A, B, or C, obtained by the reduction of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  with tin

and hydrochloric acid (see p. 1229) are heated with zinc dust and acetic acid. The dilactone nature was clearly proved by titration when it was found that one molecular proportion of the substance neutralised two molecular proportions of caustic soda. The formula just given represents this substance as a double  $\alpha$ -lactone, but, in this case also, the remark made on p. 1229 applies, and the substance may prove to be the corresponding double  $\beta$ -lactone.

### EXPERIMENTAL.

#### *Action of p-Bromophenylhydrazine on Methyl Dimethylacetoacetate.*

The methyl dimethylacetoacetate used in this investigation was obtained from Kahlbaum. Although sold as "Dimethylacetessig-aether," it is in reality the methyl and not the ethyl ester; it boils at  $174-174.2^\circ$  and has the specific gravities 1.01412 and 1.00613 at  $15^\circ/15^\circ$  and  $25^\circ/25^\circ$  respectively. The ethyl ester, first obtained by Frankland and Duppa (*Annalen*, 1866, 138, 328), boiled at  $184^\circ$  and had a specific gravity 0.9913 at  $16^\circ/16^\circ$ , and a specimen prepared by W. H. Perkin, jun., boiled at  $184.8-185^\circ$ , had a specific gravity 0.9813 at  $15^\circ/15^\circ$ , and gave on analysis  $C=60.7$ ;  $H=8.9$ , whereas theory requires  $C=60.7$ ;  $H=8.8$  per cent.

When treated with *p*-bromophenylhydrazine, methyl dimethylacetoacetate yields a crystalline condensation product, the preparation of which may conveniently be carried out as follows.

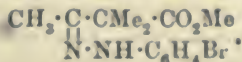
Methyl dimethylacetoacetate (2.5 c.c.) is added to a mixture of *p*-bromophenylhydrazine (3.5 grams), acetic acid (3.5 c.c.), and alcohol (10 c.c.), when, after about 12 hours, a mass of prismatic crystals will have separated. These are collected on the pump, quickly washed with alcohol, and recrystallised from a small quantity of the same solvent, when colourless crystals are obtained which melt at  $90^\circ$ . This substance is very unstable, and in one or two days decomposes with formation of a sticky, orange-coloured oil.

0.5096 gave 0.2994 AgBr. Br = 25.0.

0.5315 „ 0.3170 AgBr. Br = 25.36.

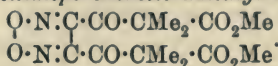
$C_{13}H_{17}O_2N_2Br$  requires Br = 25.5 per cent.

It is probable that this substance is the *p*-bromophenylhydrazone,





*Action of Nitric Acid on Methyl Dimethylacetoacetate: \* Formation of Methyl Glyoximeperoxidetetramethyldimalonylate,*



Methyl dimethylacetoacetate is not acted on by nitric acid (sp. gr. 1.4) in the cold, but on the application of heat, red fumes soon commence to be formed and are then evolved in large quantities, the reaction sometimes taking place with almost explosive violence. The operation was usually carried out as follows: about 20 c.c. of the methyl ester was placed in a round-bottomed flask of 1 litre capacity and fitted with a long, ground-in condensing tube; 10 c.c. of nitric acid (sp. gr. 1.4) were then added, and heat applied until action commenced. The source of heat was at once removed, and when, in the course of a few minutes, the reaction had partially subsided, another 10 c.c. of acid were added and the reaction allowed to proceed as before. A further addition of 10 c.c. of acid was made, and the product, which consisted of an oily and an aqueous layer, was poured into water. The yellow oil which separated gradually became semi-solid, and after 24 hours the crystalline cake was removed from the watery liquid and freed from oil, as far as possible, by pressure between calico. It was then several times crystallised from alcohol, from which it separated in colourless, transparent prisms. The amount obtained in this way was usually about 35 per cent. of the methyl dimethylmalonate employed, and experiments which were carried out with nitric acid of sp. gr. 1.5 did not give an appreciably larger yield. On analysis:

0.1620 gave 0.2925  $\text{CO}_2$  and 0.0820  $\text{H}_2\text{O}$ .  $\text{C} = 49.2$ ;  $\text{H} = 5.6$ .

0.1780 „ 0.3222  $\text{CO}_2$  and 0.0856  $\text{H}_2\text{O}$ .  $\text{C} = 49.3$ ;  $\text{H} = 5.3$ .

0.2034 „ 14.5 c.c. of nitrogen at  $16^\circ$  and 752 mm.  $\text{N} = 8.2$ .

0.2132 „ 15.2 c.c. of nitrogen at  $18^\circ$  and 769 mm.  $\text{N} = 8.3$ .

$\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  requires  $\text{C} = 49.1$ ;  $\text{H} = 5.3$ ;  $\text{N} = 8.2$  per cent.

Determinations of the molecular weight by the cryoscopic method in glacial acetic acid gave the following results:

\* When ethyl diethylacetoacetate or ethyl methylethylacetoacetate is treated with nitric acid under the same conditions as described in this section in the case of methyl dimethylacetoacetate, the reaction proceeds quite differently, and a yellow oil is formed which is lighter than water. These oils do not give any crystalline compounds when treated with phenylhydrazine, which indicates that no substance corresponding with  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  is present.

The crude product of the action of nitric acid on methyl dimethylacetoacetate is heavier than water and yields with phenylhydrazine the sparingly soluble red compound  $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$  (p. 1224).

| Substance. | Solvent. | $\Delta t.$ |          |
|------------|----------|-------------|----------|
| 0.5121     | 26.8     | 0.220°      | M = 338. |
| 0.5091     | 23.85    | 0.240°      | M = 347. |

$C_{14}H_{15}O_8N_2$  requires 342.

That this substance contains two methoxyl groups is shown by the following determinations made by Zeisel's method :

0.3320 gave 0.4596 AgI. MeO = 18.25.

0.3390 „ 0.4634 AgI. MeO = 18.0.

$C_{13}H_{14}(MeO)_2N_2O_5$  requires MeO = 18.1 per cent.

*Methyl glyoximeperoxidetetramethyldimalonylate* melts at 65°, and when heated slightly above 150° decomposes and evolves gas so rapidly as almost to cause an explosion ; it is soluble in boiling alcohol in all proportions, but rather sparingly so in cold alcohol ; it also dissolves very readily in benzene, chloroform, ether, or ethylene dichloride.

The nitric acid liquors from the preparation of this substance contain considerable quantities of dimethylmalonic acid and some oxalic acid, and these acids remain in the solid state when the diluted liquors are slowly evaporated on the water-bath. In one experiment, it was found that the amount of the mixed acids obtained in this way from 250 grams of methyl dimethylacetoacetate was as much as 60 grams.

The oily product pressed from the crystals of  $C_{14}H_{15}O_8N_2$ , as described above, has not been very carefully examined ; it dissolves in aqueous ammonia with the evolution of heat, and the solution, when acidified, deposits an oil which, after a time, partially crystallises, but if the ammoniacal solution is allowed to remain for a day or two, crystals of dimethylmalonamide separate. A suggestion as to the possible constitution of this oil is made in the introduction (p. 1218), and it may be here stated that it can only contain traces of the crystalline substance  $C_{14}H_{15}O_8N_2$ , since it does not yield the very sparingly soluble compound described on p. 1249 when it is treated with phenylhydrazine.

#### *Action of Hydrochloric Acid on the Substance $C_{14}H_{15}O_8N_2$ .*

When boiled with dilute hydrochloric acid (1 part of acid to 3 parts of water), the substance gradually dissolves, sometimes with the separation of a little tarry matter. In one experiment, 4 grams required nearly 2 days for complete solution. After cooling and filtering, the liquid, when shaken with ether, gave an extract containing dimethylmalonic acid, and the aqueous solution, when evaporated and extracted with alcohol, left a residue of ammonium chloride. The alcoholic extract, evaporated

to dryness and then dissolved in water and made alkaline, reduced Fehling's solution in the cold, indicating that hydroxylamine was probably present. It also contained a small quantity of oxalic acid. In a roughly quantitative experiment, 6 grams of  $C_{14}H_{13}O_8N_2$  gave much carbon dioxide, a small quantity of hydrocyanic acid, 1.55 grams of dimethylmalonic acid, and about 0.14 gram of oxalic acid.

*Determination of the Density, Magnetic Rotation, and Refractive Index of the Substance  $C_{14}H_{13}O_8N_2$  at Various Temperatures.*

Since this substance, after fusion, may be cooled to about  $15^\circ$  and often kept at this temperature for a long time without crystallising, it was found possible to determine the above physical constants at the ordinary temperature as well as at temperatures above its melting point. The density determinations gave the following numbers:

$$d\ 15^\circ/15^\circ = 1.2586; \quad d\ 20^\circ/20^\circ = 1.2544; \quad d\ 25^\circ/25^\circ = 1.2506.$$

Two parallel sets of determinations were then made at higher temperatures.

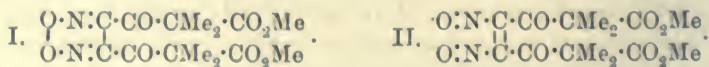
$$\begin{array}{lll} \text{I. } d\ 55^\circ/55^\circ = 1.2338; & d\ 65^\circ/65^\circ = 1.2316; & d\ 70^\circ/70^\circ = 1.2291. \\ \text{II. } d\ 55^\circ/55^\circ = 1.2302; & d\ 65^\circ/65^\circ = 1.2294; & d\ 70^\circ/70^\circ = 1.2281. \end{array}$$

If the densities between  $15^\circ$  and  $25^\circ$  be plotted out as is done in Diagram A, it will be seen that they follow a normal course, the increments becoming slightly smaller with rise of temperature.

Above  $55^\circ$ , however, the densities behave abnormally, that is to say, the increments, instead of diminishing, increase with rise of temperature. This is seen from the Diagram B (p. 1235), in which the two series of determinations I and II are plotted out.

Again, density determinations made with the same material and in the same tube, but at different times, do not give exactly the same results (see series I and II and Diagram B).

This is no doubt principally due to the tube having been heated rather longer in the one case than in the other, but all these results seem to indicate that the substance  $C_{14}H_{13}O_8N_2$  is capable of existing in two or more forms which readily pass into one another and give rise to different states of equilibrium at different temperatures. Such tautomeric modifications may, indeed, be formulated in the following way:



It is, moreover, interesting to observe that the results obtained in the determinations of the magnetic rotation and refractive index

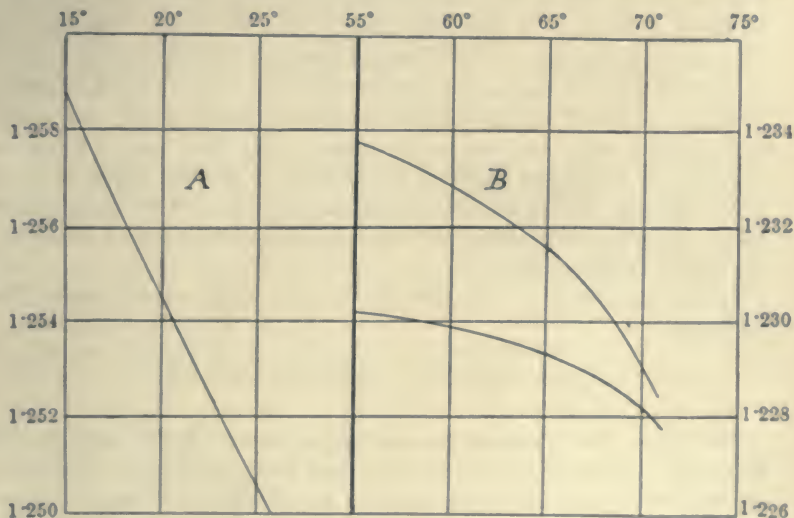


also point to the existence of different conditions of the substance at different temperatures.

The magnetic rotations were determined at two temperatures widely apart with the following results :

|                           |                     |                     |
|---------------------------|---------------------|---------------------|
| $t^\circ = 16.75^\circ$ ; | Sp. rot. = 0.9959 ; | Mol. rot. = 15.052. |
| $t^\circ = 60^\circ$ ;    | Sp. rot. = 0.9571 ; | Mol. rot. = 14.770. |

But as it was uncertain whether the substance, during the examination at the lower temperature, had had time to assume a perfect state of equilibrium, it was examined in solution, and after this had been left for several days. The solvent used was ethylene dichloride, in which the substance is very soluble, the proportion employed being



$C_{14}H_{18}O_8N_2 + 4C_2H_4Cl_2$ , or a 46.34 per cent. solution. The density of the solution at  $14^\circ/14^\circ$  was 1.2578 and the magnetic rotation was 36.993. If from this latter value the magnetic rotation of the ethylene dichloride (21.940) be deducted, 15.053 is obtained as the magnetic rotation of the substance  $C_{14}H_{18}O_8N_2$  at the ordinary temperature, a value which agrees almost exactly with that (15.052) obtained with the superfused substance. It may therefore be concluded that the superfused substance is at the ordinary temperature in the same condition of equilibrium as when dissolved in ethylene chloride. It will be seen that the difference of rotation shown above for a rise of temperature of  $43.25^\circ$  is  $-0.282$ , which is equal to a difference of  $-0.652$  for  $100^\circ$ .

It has frequently been shown that the magnetic rotation in aliphatic compounds becomes slightly smaller as the temperature rises,

but never to anything like the extent shown above (compare Trans., 1896, 69, 1063). Like the above-mentioned abnormal change in density, this unusually large fall in magnetic rotation indicates that change in constitution takes place with rise of temperature, and the nature of the values seems to point to an unsaturated substance at low temperatures, gradually passing into a saturated substance at higher temperatures. A change of this kind would take place if formula II (see p. 1234) were to gradually pass into formula I. Unfortunately, it is difficult to estimate the exact value of the magnetic rotation of a compound having a constitution represented by either of the formulæ I or II, but there is this difference, that in II there is double linking between carbon atoms, whereas this is not the case in I, and it is known that double linking usually carries with it a rise in the magnetic rotation of about 1.11 (compare Trans., 1902, 81, 292). Taking into account the position of the various groups in formula I, I have calculated that its magnetic rotation would be about 14.108, whereas that of formula II would be 15.218. The value at 16.75° was found to be 15.052, which approximately agrees with that required for an unsaturated compound (formula I), whereas at 60° the value is much lower, namely, 14.770, thus indicating that a portion of the unsaturated compound I has been converted into the saturated compound II during the rise of temperature.

In the case of the *refractive index*, the values found were the following:

$$\frac{\mu - 1}{\alpha} p. \alpha = 131.655, \beta = 135.023, \gamma = 136.988.$$

The value for formula I, calculated in the usual way, is for  $H_a = 129.8$ , which is 1.8 lower than that actually found, whereas in the case of formula II, which contains an ethylenic linking, the value should be about 132.1, so that, like the magnetic rotation, the value found at the ordinary temperature lies between these two, and thus indicates that the substance consists of a mixture of two modifications, one saturated and the other unsaturated.

#### *Action of Alkalis on the Substance $C_{14}H_{13}O_8N_2$ .*

This action was investigated under a variety of conditions in the hope of obtaining the free acid, but, in all cases, without success. When agitated with an aqueous solution of caustic potash, decomposition set in as soon as the temperature became high enough to cause the substance to fuse, and the liquid became orange-yellow, whilst methyl alcohol, ammonia, and water distilled over.

On cooling and acidifying with dilute sulphuric acid, carbon dioxide

was evolved, and, on boiling, a small quantity of hydrocyanic acid as well as a volatile acid smelling like isobutyric acid distilled over. The distillate was treated with calcium carbonate and the solution evaporated, when a readily soluble calcium salt was obtained which, with silver nitrate, yielded a crystalline silver salt.

The latter gave, on analysis, the following results, which agree with those required for silver isobutyrate :

0.2263 gave 0.1248 Ag. Ag = 55.2.

0.3036 „ 0.1679 Ag. Ag = 55.3.

$C_4H_7AgO_2$  requires Ag = 55.4 per cent.

The ethereal extract of the residue in the retort yielded a crystalline acid, and this, after recrystallisation from water, melted at  $186^\circ$  and consisted of pure dimethylmalonic acid.

0.1733 gave 0.2884  $CO_2$  and 0.099  $H_2O$ . C = 45.4 ; H = 6.3.

0.1664 „ 0.2773  $CO_2$  „ 0.0935  $H_2O$ . C = 45.4 ; H = 6.2.

$CMe_2(CO_2H)_2$  requires C = 45.4 ; H = 6.1 per cent.

The amounts of some of the principal products of the decomposition of the substance  $C_{14}H_{18}O_8N_2$  with caustic potash were roughly determined, and it was found that 10 grams of substance yielded approximately : carbon dioxide = 1.5 grams ; hydrocyanic acid = 0.05 gram ; isobutyric acid = 1.3 grams ; and dimethylmalonic acid = 4.41 grams.

From the above result, it is seen that aqueous caustic potash decomposes the compound  $C_{14}H_{18}O_8N_2$  in a fundamental manner, and it is not easy to avoid this. However, by replacing this reagent by sodium ethoxide employed under certain conditions, it has been found possible to stop the decomposition at an earlier stage and to isolate a more direct product of hydrolysis. When an alcoholic solution of  $C_{14}H_{18}O_8N_2$ , cooled until it commences to crystallise, is quickly treated with a solution of sodium ethoxide (using 1 mol. of the former to 2 mols. of the latter, and avoiding all rise of temperature) the whole dissolves, forming an orange-yellow solution. This is immediately poured into well-cooled dilute hydrochloric acid, and the cloudy solution extracted 2 or 3 times with ether ; the ethereal extract, when dried over anhydrous sodium sulphate and evaporated, finally left a syrupy liquid which, when placed over sulphuric acid, soon began to crystallise, and in about 3 days the whole had become a semi-solid mass. On mixing this with benzene and filtering at the pump, the oily impurities were easily removed, leaving a white, crystalline substance which

\* The melting point of dimethylmalonic acid is much influenced by small quantities of impurity and is usually found to be  $187^\circ$  (Beilstein gives  $117^\circ$ , but this is obviously a mistake). When, however, the acid is prepared from its pure zinc salt, it melts sharply at  $190^\circ$ .



melted at about  $140^{\circ}$ ; this product separated from toluene in stellate groups melting at  $142-143^{\circ}$ .

0.1535 gave 0.2204  $\text{CO}_2$  and 0.0653  $\text{H}_2\text{O}$ .  $\text{C} = 39.2$ ;  $\text{H} = 4.7$ .

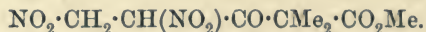
0.1707 „ 0.2458  $\text{CO}_2$  „ 0.0723  $\text{H}_2\text{O}$ .  $\text{C} = 39.3$ ;  $\text{H} = 4.7$ .

0.2235 „ 22 c.c. of nitrogen at  $18^{\circ}$  and 777 mm.  $\text{N} = 11.6$ .

0.1218 „ 12.4 c.c. „ „  $14.4^{\circ}$  and 738 mm.  $\text{N} = 11.6$ .

$\text{C}_8\text{H}_{12}\text{O}_7\text{N}_2$  requires  $\text{C} = 38.9$ ;  $\text{H} = 4.8$ ;  $\text{N} = 11.3$  per cent.

A methoxyl determination by Zeisel's method gave the following results: 0.3630 gave 0.3258  $\text{AgI}$ , corresponding with 11.8 per cent. of  $\text{MeO}$ , whereas the formula  $\text{C}_6\text{H}_9\text{N}_2\text{O}_5$  ( $\text{CO}_2\text{Me}$ ) contains 12.5 per cent. of  $\text{MeO}$ . If the aqueous solution of this substance is warmed, it decomposes with separation of an oily acid which has not been further investigated. It has been suggested in the introduction that this curious substance,  $\text{C}_8\text{H}_{12}\text{O}_7\text{N}_2$ , is produced by the simultaneous oxidising and hydrolysing action of the sodium ethoxide, and that it has the formula



It has therefore been provisionally named *methyl  $\alpha\beta$ -dinitroethane-dimethylmalonylate*, and such a substance would, of course, possess acid properties. When a cold concentrated alcoholic solution of this substance is treated with an alcoholic solution of phenylhydrazine, a pasty, crystalline, buff or pale yellow mass immediately separates, but this soon assumes an orange-red colour. If the solution is less concentrated, no crystals form at first, but the liquid soon becomes orange and then red, and bright red crystals are subsequently deposited in quantity. After recrystallising from alcohol, the substance gave the following results:

0.1457 gave 0.2958  $\text{CO}_2$  and 0.0730  $\text{H}_2\text{O}$ .  $\text{C} = 55.3$ ;  $\text{H} = 5.5$ .

0.1659 „ 26.1 c.c. of nitrogen at  $17^{\circ}$  and 770 mm.  $\text{N} = 18.4$ .

$\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$  requires  $\text{C} = 55.3$ ;  $\text{H} = 5.3$ ;  $\text{N} = 18.4$  per cent.

This substance is the same as that which is produced when the compound  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  is treated with phenylhydrazine (p. 1249), and in its formation, according to the equation



some of the phenylhydrazine must have acted as a reducing agent.

The reaction does not take place quantitatively because the alcoholic mother liquors contain a considerable quantity of a viscid, brown, tarry matter. It is also curious that, when treated with semicarbazide, the compound  $\text{C}_8\text{H}_{12}\text{O}_7\text{N}_2$  appears to yield the substance  $\text{C}_9\text{H}_{15}\text{O}_6\text{N}_5$  described on p. 1255.

When the compound  $C_8H_{12}O_7N_2$  is dissolved in warm ether and mixed with enough benzene to induce crystallisation, a remarkable change takes place, and, on cooling, a white, crystalline substance separates in warty masses which melt at  $165-168^\circ$ . After a time, the mother liquors usually deposit some of the unchanged substance. The new substance crystallises from boiling toluene, in which it is sparingly soluble, in small, flat prisms which melt at  $169^\circ$ .

Considerable difficulty was experienced in analysing this substance owing to the fact that, when heated, it decomposed suddenly and with a rapid evolution of gas.

0.1439 gave 0.2402  $CO_2$  and 0.0638  $H_2O$ .  $C=45.5$ ;  $H=4.9$ .

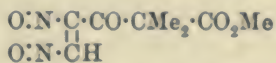
0.1595 „ 0.2635  $CO_2$  „ 0.0695  $H_2O$ .  $C=45.0$ ;  $H=4.8$ .

0.1742 „ 19.7 c.c. of nitrogen at  $19^\circ$  and 752 mm.  $N=12.8$ .

0.1617 „ 18.5 c.c. „  $20^\circ$  „ 757 mm.  $N=13.0$ .

$C_8H_{10}O_5N_2$  requires  $C=44.8$ ;  $H=4.7$ ;  $N=13.1$  per cent.

It is explained in the introduction that this substance probably has a constitution represented either by the formula



or by the tautomeric modification of this formula, and it was therefore named *methyl dinitrosoethylenedimethylmalonylate*. It is readily soluble in alcohol and ether, and does not appear to react with phenylhydrazine. When treated with solutions of dilute alkalis, or even of sodium carbonate, it dissolves, forming lemon-yellow solutions from which a plastic mass separates on the addition of alkalis. The basicity of the substance was determined by titration with decinormal caustic soda, when it was found that 0.1849 required for neutralisation 0.034 NaOH, whereas this amount of a monobasic acid  $C_8H_{10}O_5N_2$  should neutralise 0.0343 NaOH.

The benzene washings of the crystals of the substance  $C_8H_{12}O_7N_2$ , when allowed to evaporate spontaneously, leave a syrupy mass of an acid character, which becomes oily on the addition of a little water, and almost entirely dissolves if a considerable quantity of water is used. The nature of this substance was determined as follows: the syrupy mass was dissolved in a good deal of water, the solution gently heated with calcium carbonate on the water-bath, and, after the effervescence had ceased, filtered from a little tarry matter. On evaporating the filtrate to a small bulk, crystalline crusts separated in quantity, and were collected at the pump and washed with a little hot water. By concentrating the mother liquors, further quantities of the same salt were obtained, and the combined crops were then

recrystallised by evaporating their aqueous solution to a small bulk as before.

0.3843 gram of the salt, after drying over sulphuric acid *in vacuo*, lost, at 100°, 0.0381 gram.  $H_2O = 9.9$ .

0.3462 gram, dried at 100°, gave 0.1370  $CaSO_4$ .  $Ca = 11.6$ .  
 $(CO_2Me \cdot CMe_2 \cdot CO_2)_2Ca, 2H_2O$  requires  $H_2O = 9.8$ , and the anhydrous salt contains  $Ca = 11.5$  per cent.

This salt is therefore probably *calcium methyl dimethylmalonate*, and, as this compound had not previously been described, it was thought necessary, in order to establish its identity, to prepare it directly from methyl dimethylmalonate, this being accomplished in the following way: methyl dimethylmalonate (56 grams) was dissolved in 80 c.c. of alcohol and mixed with sodium (9.2 grams) dissolved in 160 c.c. of alcohol, all rise of temperature being avoided by carefully cooling under the tap. After remaining for 12 hours, a considerable quantity of a salt, similar in appearance to alumina, had separated which was evidently the disodium salt of dimethylmalonic acid; this was collected at the pump, an operation which was very tedious, owing to the gelatinous nature of the precipitate. The filtrate was evaporated to a small bulk on the water-bath and extracted twice with ether to remove any unchanged ester. The aqueous solution was then strongly acidified with hydrochloric acid and extracted twice with ether, the ethereal solution was dried with anhydrous sodium sulphate and evaporated, and in this way 30 grams of a colourless syrup were obtained which consisted of almost pure methyl hydrogen dimethylmalonate.

This acid is moderately soluble in water, and, if heated alone, it decomposes with evolution of carbon dioxide and formation of an oil which is obviously methyl isobutyrate. When heated with ammonia in a sealed tube at 100°, the product, on acidifying and extracting with ether, yields a crystalline mass consisting evidently of *dimethylmalonamic acid*,  $CO_2H \cdot CMe_2 \cdot CONH_2$ .

*The Calcium Salt.*—In order to prepare this salt, a quantity of the acid was dissolved in water and heated with calcium carbonate; the filtered liquid was then evaporated to a small bulk on the water-bath until the salt separated in crystalline crusts, which were collected, washed with hot water, and analysed:

0.4875 gram, dried over sulphuric acid *in vacuo*, lost 0.0483 gram at 100°.  $H_2O = 9.9$ .

0.4393 gram of the anhydrous salt gave 0.1786  $CaSO_4$ .  $Ca = 11.9$ .  $(CO_2Me \cdot CMe_2 \cdot CO_2)_2Ca, 2H_2O$  requires  $H_2O = 9.8$ , and the anhydrous salt contains  $Ca = 11.5$  per cent.



This salt was identical with that obtained from the product of the action of sodium ethoxide on the substance  $C_{14}H_{15}O_5N_2$  in the manner described above.

*Action of Ammonia on the Substance  $C_{14}H_{15}O_5N_2$*

When the finely-powdered substance,  $C_{14}H_{15}O_5N_2$ , is shaken with strong aqueous ammonia, it dissolves with evolution of sufficient heat to raise the temperature to the boiling point. The orange-coloured solution soon becomes paler in tint, and often in the course of 2 hours, crystals begin to separate. After remaining for 24 hours, these were collected, recrystallised from boiling water, and analysed.

0.1645 gave 0.2786  $CO_2$  and 0.1131  $H_2O$ .  $C = 46.2$ ;  $H = 7.6$ .

0.2125 „ 40 c.c. of nitrogen at  $17^\circ$  and 754 mm.  $N = 21.7$ .

$C_5H_{10}O_2N_2$  requires  $C = 46.1$ ;  $H = 7.7$ ;  $N = 21.5$  per cent.

This substance is *dimethylmalonamide*,  $NH_2 \cdot CO \cdot CMe_2 \cdot CO \cdot NH_2$ ; it melts at  $263^\circ$ , and when obtained under the above conditions the yield is sometimes nearly 30 per cent. of the  $C_{14}H_{15}O_5N_2$  employed. If, however, the reaction is made to take place slowly, by keeping the mixture at  $0^\circ$ , the substance  $C_{14}H_{15}O_5N_2$  dissolves very slowly and solution is not complete until after several hours. The residue obtained by evaporating the somewhat viscid, orange-coloured solution *in vacuo*, when treated with cold water, yields only a small quantity of dimethylmalonamide, and the filtrate, when subsequently concentrated under diminished pressure, furnishes a small amount of a beautifully crystalline substance which is sparingly soluble in cold water and melts at  $129^\circ$ . Unfortunately, the yield of this new substance is very small, and it could therefore not be analysed and further investigated. It may possibly be similarly constituted to the substance  $C_{20}H_{24}O_5N_4$  (p. 1242), which is obtained by the action of aniline on the compound  $C_{14}H_{15}O_5N_2$ .

When dry ammonia gas was passed into the solution of  $C_{14}H_{15}O_5N_2$  in ten parts of dry ether, the liquid became at first pale yellow and then darker, and a viscid, yellow layer separated, sufficient heat being evolved to cause the ether to boil. When the whole had been saturated with the gas, the ethereal layer was decanted from the viscid, yellow product and evaporated to a small bulk. The substance obtained when twice crystallised from ether separated in flat needles.

0.1674 gave 0.3060  $CO_2$  and 0.1152  $H_2O$ .  $C = 49.8$ ;  $H = 7.6$ .

0.2522 „ 22.3 c.c. of nitrogen at  $16^\circ$  and 742 mm.  $N = 9.9$ .

$C_6H_{11}O_3N$  requires  $C = 49.7$ ;  $H = 7.6$ ;  $N = 9.6$  per cent.

This substance is *methyl dimethylmalonamate*,  $\text{CO}_2\text{Me}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$ ; it melts at  $85\text{--}86^\circ$  and distils apparently without decomposition. The viscid, yellow product mentioned above, after remaining for some weeks, deposited crystals apparently of two kinds, but not in large quantities. These crystals, which are very soluble in water, have not been further investigated.

*Preparation of Dimethylmalonamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$ .—As the amide (m. p.  $263^\circ$ ) obtained by the action of ammonia on the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  melts at a temperature much higher than that given by L. T. Thorne (Trans., 1881, 39, 545), namely,  $196\text{--}198^\circ$ , it became necessary to investigate this matter. Thorne prepared his amide by the action of alcoholic ammonia on ethyl dimethylmalonate at  $120^\circ$  in a sealed tube, but the yield was very small. I also found that when methyl dimethylmalonate is heated with alcoholic ammonia in a sealed tube at  $100^\circ$ , a small amount only of a crystalline substance is obtained. If, however, the methyl ester is heated at  $100^\circ$  with strong aqueous ammonia for 2 hours, the tube is found to be filled with a mass of glistening crystals. It was subsequently discovered that the same result is brought about by simply shaking with aqueous ammonia. The dimethylmalonamide thus obtained melted, after recrystallisation, at  $263^\circ$  uncorr. or  $269^\circ$  corr. Since these experiments were made, Emil Fischer (*Ber.*, 1902, 35, 851, 855) has experimented on the action of ammonia on ethyl dimethylmalonate, and by heating it in a sealed tube with alcoholic ammonia at  $145^\circ$  for 30 hours obtained only 2.6 per cent. of the amide. He gives the melting point as  $261^\circ$  (corr.), which is rather lower than that obtained by me. It is curious that the yield is so small when alcoholic ammonia is used. Fischer considers that Thorne's compound was monomethylmalonamide.

*Action of Aniline on the Substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .*

When a cold solution of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  in twice its weight of benzene is mixed with an equal weight of aniline (that is, about 3.5 molecular proportions of aniline to 1 of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ ), the solution becomes yellow, and the temperature gradually rises about  $16^\circ$ , and, in about an hour's time, groups of prismatic crystals begin to separate; after 24 hours, these are collected at the pump and washed with benzene. In one experiment, 9 grams of this substance were obtained from 10 grams of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ , in another, only 7.2, and at other times much less, and it seems that a very slight alteration in the conditions, especially with regard to temperature, has a very marked influence on

the amount of this substance which is formed.\* As considerable difficulty was experienced in assigning a formula to this substance, several analyses were made, the material used in each being obtained from a different experiment.

|        |      |        |                  |                       |         |                   |                |
|--------|------|--------|------------------|-----------------------|---------|-------------------|----------------|
| 0.1411 | gave | 0.3097 | CO <sub>2</sub>  | and                   | 0.0791  | H <sub>2</sub> O. | C=59.9; H=6.2. |
| 0.1597 | "    | 0.3512 | CO <sub>2</sub>  | "                     | 0.0882  | H <sub>2</sub> O. | C=60.0; H=6.1. |
| 0.1486 | "    | 0.3275 | CO <sub>2</sub>  | "                     | 0.0807  | H <sub>2</sub> O. | C=60.1; H=6.0. |
| 0.1597 | "    | 19.6   | c.c. of nitrogen | at 21° and 763 mm.    | N=14.0. |                   |                |
| 0.1679 | "    | 21.2   | c.c.             | " " 18.5° and 742 mm. | N=14.2. |                   |                |

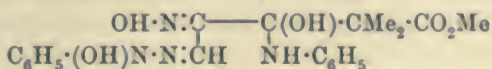
Other analyses gave numbers closely agreeing with these.

C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub> requires C=60.0; H=6.0; N=14.0 per cent.

This substance melts at about 108—110° with decomposition, and is readily soluble in ether and in alcohol, but sparingly soluble in benzene; it cannot be recrystallised without decomposition.

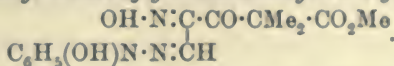
The molecular weight and formula of this substance could, however, be established beyond doubt by the study of the corresponding compound, which was obtained by acting on C<sub>14</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub> with *p*-chloro-aniline instead of with aniline (p. 1246).

As the result of the study of the decomposition products of this substance, the constitution



was assigned to it in the introduction, and the substance was named methyl dianilinoglyoximedimethylmalonylate.

*Methyl Anilinoglyoximedimethylmalonylate,*



When the dianilino-compound C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub> is treated, in the cold, with very dilute hydrochloric acid, it decomposes, forming aniline hydrochloride and yielding a white substance.

\* If the temperature is kept at about 0°, a different decomposition takes place, and no crystalline substance separates. That there has been a change is shown by the fact that a subsequent rise of temperature does not lead to a separation of crystals. If the reacting substances are mixed at 20°, the temperature rises to 36°, and a crop of crystals of the substance C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub> separates on cooling. In a third experiment, in which the aniline was added to the boiling benzene solution of the substance C<sub>14</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub>, the reaction caused the solution to continue boiling for some time and, on cooling, the substance C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub> (about 15 per cent.) first separated and then a crop of crystals of C<sub>14</sub>H<sub>17</sub>O<sub>8</sub>N<sub>2</sub> the yield being about 25 per cent. (see p. 1244).



The latter was collected, washed with water, dried, and recrystallised from benzene, from which it separates in groups of slender needles radiating from a common point, and which, when dried, melt at  $137^{\circ}$ . The same substance may be obtained by acting on  $C_{14}H_{18}O_5N_2$  with aniline at  $80^{\circ}$  (see footnote, p. 1243), or simply by boiling the compound  $C_{20}H_{24}O_5N_4$  with benzene, when a pulp of white crystals is produced; these dissolve, and, on cooling, the solution deposits needles which melt as before at  $137^{\circ}$ . The aniline removed during the decomposition remains in the benzene. After twice recrystallising from benzene, the substance melting at  $137^{\circ}$ , which has been named *methyl anilinoglyoximedimethylmalonate*, was analysed with the following results:

0.1431 gave 0.2855  $CO_2$  and 0.0740  $H_2O$ .  $C = 54.4$ ;  $H = 5.7$ .

0.1573 „ 0.3148  $CO_2$  „ 0.0798  $H_2O$ .  $C = 54.4$ ;  $H = 5.7$ .

0.1481 „ 17.8 c.c. of nitrogen at  $22^{\circ}$  and 764 mm.  $N = 13.7$ .

0.1891 „ 21.6 c.c. „ „  $13^{\circ}$  „ 765 mm.  $N = 13.9$ .

$C_{14}H_{17}O_5N_3$  requires  $C = 54.7$ ;  $H = 5.5$ ;  $N = 13.7$  per cent.

This substance dissolves readily in alcohol and ether, but is sparingly soluble in benzene and still less so in light petroleum.

The melting point is not quite sharp, and varied in different preparations between  $137^{\circ}$  and  $140^{\circ}$ . It exhibits both basic and acid properties. If the finely-divided substance is gently warmed with dilute hydrochloric acid, it dissolves, and the solution slowly deposits nodular crystals of the *hydrochloride*. These were collected at the pump, washed with dilute hydrochloric acid, dried *in vacuo* over caustic potash, and analysed.

0.3543 gave 0.1456  $AgCl$ .  $Cl = 10.2$ .

$C_{14}H_{17}O_5N_3.HCl$  requires  $Cl = 10.3$  per cent.

This salt may also be prepared by adding concentrated hydrochloric acid to the alcoholic solution of the substance  $C_{14}H_{17}O_5N_3$  and allowing the solution to evaporate over sulphuric acid *in vacuo*; it is thus obtained in good-sized, transparent crystals.

The hydrochloride, which does not give a crystalline double salt with platinic chloride, is readily soluble in water; its aqueous solution has a very bitter taste, and gives a deep blue coloration with ferric chloride. The base is precipitated from the solution of hydrochloride by caustic alkali, but quickly dissolves in any excess of the reagent; solutions of sodium carbonate or ammonia produce the same result. The base is conveniently prepared from its hydrochloride by adding sodium acetate to the solution of this salt; the precipitate which slowly separates, when collected and crystallised from benzene, yields needle-shaped crystals which melt at about  $134^{\circ}$ .

0.1491 gave 0.2967  $\text{CO}_2$  and 0.0753  $\text{H}_2\text{O}$ .  $\text{C} = 54.3$ ;  $\text{H} = 5.6$ .

0.1625 „ 18.8 c.c. of nitrogen at  $13^\circ$  and 756 mm.  $\text{N} = 13.6$ .

$\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_3$  requires  $\text{C} = 54.7$ ;  $\text{H} = 5.5$ ;  $\text{N} = 13.7$  per cent.

These results indicate that the substance had not undergone any alteration in constitution on treatment with hydrochloric acid. The *sulphate* may be readily prepared by dissolving the base in dilute sulphuric acid and allowing the solution to evaporate spontaneously. It is thus obtained in long, transparent prisms which are readily soluble in water and dissolve in concentrated sulphuric acid with a bluish-violet colour which, however, soon changes to a pale brown or drab. The aqueous solution gives a blue coloration on the addition of ferric chloride.

*Methyl Dimethylmalonanilate*,  $\text{CO}_2\text{Me} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .—As explained in the introduction (p. 1222), this substance is always produced along with the compound  $\text{C}_{20}\text{H}_{24}\text{O}_5\text{N}_4$  when aniline acts on  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ , and it is contained in the benzene mother liquors from which the former has crystallised (p. 1242). These benzene liquors were allowed to evaporate spontaneously and the crystalline residue was heated on the water-bath with dilute hydrochloric acid in order to dissolve excess of free aniline and also to convert small quantities of the substance  $\text{C}_{20}\text{H}_{24}\text{O}_5\text{N}_4$  which might be present into aniline and the base  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_3$ , when both would dissolve as hydrochlorides. The solid melted during this treatment, but the oil, which was insoluble in the dilute hydrochloric acid, solidified on cooling. The crystals were left in contact with porous porcelain for a few days in order to remove the oily matter with which they were contaminated, and were then twice recrystallised from light petroleum (b. p.  $80\text{--}90^\circ$ ), the viscid oily product which first separated being removed by decantation and the liquid then set aside to crystallise. The crystals were further purified by two crystallisations from a mixture of equal parts of benzene and light petroleum. The new substance separates in colourless leaflets with a satiny lustre and the amount obtained, in an experiment in which 10 grams of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  had been treated with aniline, was 3.7 grams.

0.1351 gave 0.3243  $\text{CO}_2$  and 0.0898  $\text{H}_2\text{O}$ .  $\text{C} = 65.4$ ;  $\text{H} = 7.4$ .

0.1540 „ 0.3684  $\text{CO}_2$  and 0.0966  $\text{H}_2\text{O}$ .  $\text{C} = 65.1$ ;  $\text{H} = 7.0$ .

0.1916 „ 10 c.c. of nitrogen at  $19^\circ$  and 762 mm.  $\text{N} = 6.5$ .

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$  requires  $\text{C} = 65.2$ ;  $\text{H} = 6.8$ ;  $\text{N} = 6.3$  per cent.

*Methyl dimethylmalonanilate* melts at  $80^\circ$  and is readily soluble in alcohol, ether and benzene, but sparingly so in cold light petroleum. When an alcoholic solution is warmed with alcoholic soda and the liquid, after diluting with water, is acidified with hydrochloric acid, an oil is deposited which solidifies on cooling. This substance

crystallises from alcohol, in which it is very readily soluble, in well-defined prisms which melt at  $133^{\circ}$ , and there can be no doubt that it is dimethylmalonanilic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , produced by the simple hydrolysis of the methyl ester.

*Action of p-Chloroaniline on the Substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ .*

As already mentioned in the introduction (p. 1223), these experiments were made with the object of establishing the molecular weights, as well as obtaining further evidence of the nature of the substances which are produced when aniline acts on  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ . On mixing cold solutions of 10 grams of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  and 15 grams of *p*-chloroaniline in 10 and 35 c.c. of benzene respectively, a yellow liquid was obtained which, after 24 hours, became filled with pale pink crystals. These, when collected at the pump, washed with benzene, and allowed to remain in the air until dry, melted at  $118$ — $120^{\circ}$ . It was found possible to recrystallise this substance by dissolving it in dry, cold ether, in which it is moderately readily soluble, and then adding light petroleum (b. p.  $80$ — $90^{\circ}$ ) until a slight cloudiness was produced.

Brilliant prisms gradually separated, often in stellate groups; these melted at  $117$ — $120^{\circ}$  and were analysed with the following results:

0.1360 gave 0.2563  $\text{CO}_2$  and 0.0580  $\text{H}_2\text{O}$ .  $\text{C} = 51.3$ ;  $\text{H} = 4.6$ .

0.1371 „ 0.2576  $\text{CO}_2$  and 0.0642  $\text{H}_2\text{O}$ .  $\text{C} = 51.3$ ;  $\text{H} = 4.5$ .

0.1781 „ 18.5 c.c. of nitrogen at  $16^{\circ}$  and 750 mm.  $\text{N} = 12.1$ .

0.5364 „ 0.3198  $\text{AgCl}$ .  $\text{Cl} = 14.7$ .

$\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_4\text{Cl}_2$  requires  $\text{C} = 51.1$ ;  $\text{H} = 4.6$ ;  $\text{N} = 11.9$ ;  $\text{Cl} = 15.1$  per cent.

This substance, which is therefore exactly analogous to the compound  $\text{C}_{20}\text{H}_{24}\text{O}_5\text{N}_4$ , obtained by acting on the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  with aniline, has accordingly been named *methyl di-p-chlorodianilino-glyoximedimethylmalonylate*.

*Methyl p-Chloroanilinoglyoximedimethylmalonylate,  $\text{C}_{14}\text{H}_{16}\text{O}_5\text{N}_3\text{Cl}$ .*

This substance is produced when the dichlorodianilino-compound just described is decomposed by hydrochloric acid or simply boiled with benzene, the conditions of experiment being exactly similar to those already described in the case of the corresponding dianilino-compound (p. 1242); it is also formed directly from  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  when the amount of *p*-chloroaniline employed is insufficient for the production of the dichlorodianilino-compound. It melts at  $140^{\circ}$  and crystallises from benzene in small prisms, but is obtained in the form of glistening needles when its solution in ether is mixed with just sufficient light petroleum to produce a cloudiness, and then allowed to remain for some



hours. It is readily soluble in alcohol and in ether, but sparingly so in cold benzene and light petroleum; its alcoholic solution gives a pale blue coloration with ferric chloride.

0.1463 gave 0.2651  $\text{CO}_2$  and 0.0663  $\text{H}_2\text{O}$ .  $\text{C} = 49.4$ ;  $\text{H} = 5.0$ .

0.5138 „ 0.2153  $\text{AgCl}$ .  $\text{Cl} = 10.4$ .

0.1937 „ 20.5 c.c. of nitrogen at  $19^\circ$  and 762 mm.  $\text{N} = 12.2$ .

$\text{C}_{14}\text{H}_{16}\text{O}_5\text{N}_3\text{Cl}$  requires  $\text{C} = 49.2$ ;  $\text{H} = 4.7$ ;  $\text{Cl} = 10.4$ ;  $\text{N} = 12.3$  per cent.

The *hydrochloride* is obtained in transparent well-defined crystals when a solution of the substance in alcohol is saturated with hydrogen chloride and then allowed to evaporate over sulphuric acid under a bell-glass, care being taken that hydrogen chloride is always present. The crystals for analysis were quickly drained, pressed between filter paper, and then dried, first over sulphuric acid in an atmosphere of hydrogen chloride, and afterwards for a couple of hours over caustic potash under diminished pressure.

0.5129 gave 0.3844  $\text{AgCl}$ .  $\text{Cl} = 18.6$ .

$\text{C}_{14}\text{H}_{16}\text{O}_5\text{N}_3\text{Cl} \cdot \text{HCl}$  requires  $\text{Cl} = 18.8$  per cent.

When treated with water, the transparent crystals of the hydrochloride become opaque owing to dissociation into the base and hydrochloric acid, a change which takes place much more readily than is the case with the hydrochloride of the corresponding anilino-compound described on p. 1244.

*Methyl Dimethylmalon-p-chloroanilate*,  $\text{CO}_2\text{Me} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$ .

The benzene mother liquors from the preparation of  $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_4\text{Cl}_7$  (p. 1246) deposited, on spontaneous evaporation, a crystalline residue which was rubbed with a little cold benzene and then washed with small quantities of the same solvent. The crude product, after drying, weighed 4.5 grams from an operation in which 10 grams of  $\text{C}_{14}\text{H}_{15}\text{O}_5\text{N}_2$  had been treated with *p*-chloroaniline; it was purified by dissolving in boiling ether and then allowing the solution to cool and evaporate somewhat, and was thus obtained in flat, transparent prisms melting at  $88-90^\circ$ . A second recrystallisation from a mixture of ether and light petroleum raised the melting point to  $90-91^\circ$ .

0.1437 gave 0.2962  $\text{CO}_2$  and 0.0741  $\text{H}_2\text{O}$ .  $\text{C} = 56.2$ ;  $\text{H} = 5.7$ .

0.5297 „ 0.2970  $\text{AgCl}$ .  $\text{Cl} = 13.9$ .

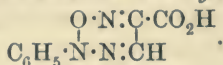
0.2101 „ 10.0 c.c. of nitrogen at  $17^\circ$  and 767 mm.  $\text{N} = 5.7$ .

$\text{C}_{12}\text{H}_{14}\text{O}_5\text{NCl}$  requires  $\text{C} = 56.3$ ;  $\text{H} = 5.5$ ;  $\text{Cl} = 13.8$ ;  $\text{N} = 5.5$  per cent.

This substance, which dissolves readily in alcohol and in ether, is much less soluble in benzene and only sparingly so in light petroleum;

it appears to distil with very little decomposition. When the alcoholic soda solution of the substance is gently warmed, then diluted with water, and acidified with dilute hydrochloric acid, a substance is obtained which crystallises from benzene in needles and melts at  $160^{\circ}$ . This is, doubtless, dimethylmalon-*p*-chloroanilic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ .

*Phenylisotriazoxolecarboxylic Acid,*



When the substance  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_3$  (p. 1244) is treated with dilute caustic soda, it dissolves to an orange-coloured solution which becomes paler after a short time. If, when the colour is at its maximum, the solution is poured into dilute hydrochloric acid, it becomes redder and soon deposits a small quantity of a dark red, crystalline precipitate, whilst the unchanged substance and other decomposition products remain dissolved. The amount of the new substance obtained in this way was usually very small, and it was only by working under special conditions that it was ultimately found possible to prepare it in quantities sufficient for examination. The substance  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_3$  (0.4 gram) is dissolved in 2 c.c. of warm alcohol in a test-tube; the solution is then cooled and quickly mixed with 1 c.c. of a 10 per cent. solution of alcoholic soda. The liquid rapidly acquires an orange colour, very like strong potassium bichromate solution in intensity, and the temperature rises about  $5^{\circ}$ . In three quarters of a minute from the time of mixing, the liquid is poured into a few c.c. of dilute hydrochloric acid (1 of acid to 3 of water), when a scarlet solution is produced which rapidly becomes semi-solid owing to the separation of a mass of minute, red crystals. The products from several similar operations are diluted with water, filtered at the pump, and the residue repeatedly washed with water. Under the microscope, the substance is seen to be perfectly uniform and, after drying *in vacuo* for several days, it was analysed with the following results:

0.0980 gave 0.1886  $\text{CO}_2$  and 0.0336  $\text{H}_2\text{O}$ . C = 52.4; H = 3.8.

0.1430 „ 0.2776  $\text{CO}_2$  and 0.0504  $\text{H}_2\text{O}$ . C = 52.9; H = 3.9.

0.1741 „ 31.2 c.c. of nitrogen at  $23^{\circ}$  and 762 mm. N = 20.3.

$\text{C}_9\text{H}_7\text{O}_3\text{N}_3$  requires C = 52.7; H = 3.6; N = 20.5 per cent.

*Phenylisotriazoxolecarboxylic acid* melts at  $155^{\circ}$  with decomposition and slight explosion. It is somewhat soluble in boiling water and crystallises, on cooling, in microscopic needles, but a considerable amount is decomposed by this treatment. It is sparingly soluble in

ether, but readily so in alcohol, and also in acetone, and if the solution in the last-named solvent is allowed to evaporate spontaneously the substance is deposited in thick, garnet-red crystals. The yield obtained by the foregoing process is about 40 per cent. of the  $C_{14}H_{17}O_5N_3$  employed and, in its preparation, the dianilino-compound,  $C_{20}H_{24}O_5N_4$  (p. 1243), and sodium ethoxide of relatively the same strength may be employed instead of alcoholic soda, but the best results have always been obtained under the conditions described on p. 1248. The aqueous washings from the preparation of the red acid give a precipitate of the unchanged substance  $C_{14}H_{17}O_5N_3$  on acidifying, and the liquid contains a small quantity of a volatile acid which, as the analysis of the barium salt showed, is doubtless isobutyric acid.

*The Silver Salt*,  $C_9H_6O_3N_3Ag$ .—When alcoholic solutions of silver nitrate and the acid are mixed, the silver salt separates at once as an orange-red, apparently crystalline precipitate, which was collected, washed with alcohol, and dried over sulphuric acid *in vacuo*. As the salt explodes on heating, it could not be analysed in the usual manner; it was weighed into a porcelain crucible, moistened with alcohol and a few drops of sulphuric acid, and heated, gently at first, but afterwards over the blowpipe.

0.3286 gave 0.1136 Ag.  $Ag = 34.6$  per cent.

$C_9H_6O_3N_3Ag$  requires  $Ag = 34.6$  per cent.

The acid dissolves in alkali carbonates with effervescence, and is converted into a sparingly soluble salt when treated with potassium acetate. The orange-red solutions of the acid in caustic alkalis soon become pale owing to decomposition.

The substance  $C_{14}H_{16}O_5N_3Cl$  (p. 1246), when treated with caustic soda, yields the corresponding acid, which crystallises from acetone in large, red crystals and melts with decomposition at about  $145^\circ$ .

#### *Action of Phenylhydrazine on the Substance $C_{14}H_{18}O_8N_7$*

If a warm concentrated alcoholic solution of the substance  $C_{14}H_{18}O_8N_7$  is mixed with acetic acid and a strong alcoholic solution of phenylhydrazine, the liquid quickly becomes orange-red and a violent action takes place, the temperature quickly rising to the boiling point. After about an hour, red crystals begin to form and gradually increase in quantity, but, to obtain this new substance in a pure condition, it is necessary to moderate the reaction by using more dilute solutions and to prevent the rise of temperature. After many experiments, the following method of preparation was found to give good results.

The substance  $C_{14}H_{18}O_8N_7$  (7 grams) is dissolved in 70 c.c. of warm



alcohol and the solution cooled until crystallisation just commences. A mixture of phenylhydrazine (5 grams), glacial acetic acid (5 c.c.), and alcohol (10 c.c.) is then gradually added, care being taken to avoid any rise of temperature. After 12 hours, about 4 grams of a brilliant red, crystalline substance separates, which was prepared for analysis by washing rapidly with alcohol and drying over sulphuric acid.

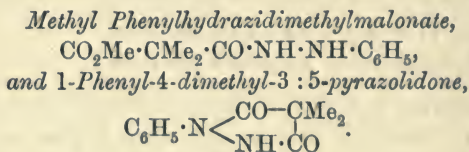
0.1704 gave 0.3468 CO<sub>2</sub> and 0.0820 H<sub>2</sub>O. C=55.5; H=5.4.

0.1432 „ 0.2917 CO<sub>2</sub> „ 0.0705 H<sub>2</sub>O. C=55.5; H=5.5.

0.1743 „ 27.4 c.c. of nitrogen at 16° and 761 mm. N=18.3.

C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub> requires C=55.3; H=5.3; N=18.4 per cent.

This substance, which has been named *methyl phenylaminoisotriazoxoledimethylmalonylate*, and the constitution of which is discussed in the introduction (p. 1226), melts at 154° if prepared exactly as described above. If, however, it is recrystallised from alcohol, in which it is sparingly soluble, the melting point sinks to about 139°, but the ester does not apparently undergo any change in composition, and it is therefore possible that this substance is capable of existing in dimorphous forms.



The first of these is contained in the red mother liquors from the substance C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub> (p. 1249), and is left behind in a very crude state, as a crystalline mass mixed with tar, when these liquors are allowed to evaporate spontaneously. Much of the tar was removed by washing with cold ether, and the residue was then digested with benzene, which dissolved the new substance and left undissolved most, but not all, of the substance C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub>, which is always present. The filtered solution gradually deposited yellowish-white crystals which were collected before they became mixed with the red crystals of the substance C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>N<sub>4</sub>; it is curious that, although the latter is so sparingly soluble in benzene, it crystallises so slowly that it actually separates after the former much more soluble substance. After recrystallising twice from benzene and five or six times from alcohol, colourless needles were obtained which, on analysis, gave the following results:

0.1381 gave 0.3085 CO<sub>2</sub> and 0.0858 H<sub>2</sub>O. C=60.9; H=6.9.

0.1806 „ 18.5 c.c. of nitrogen at 18.5° and 761 mm. N=12.0.

C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub> requires C=61.0; H=6.8; N=11.9 per cent.

*Methyl phenylhydrazidimethylmalonate* melts at  $111^{\circ}$  and is readily soluble in hot benzene, but rather sparingly so in the cold solvent. It dissolves readily in boiling alcohol, and separates slowly, on cooling, in hard masses of crystals. When boiled with dilute caustic potash,\* it soon dissolves and, on adding hydrochloric acid, a copious, white precipitate of *phenyldimethylpyrazolidone* (see p. 1225) is produced. This was collected, washed, dried, and recrystallised from alcohol, from which it separates in transparent prisms melting at  $177^{\circ}$ .

0.1625 gave 0.3872  $\text{CO}_2$  and 0.0876  $\text{H}_2\text{O}$ .  $\text{C} = 64.9$ ;  $\text{H} = 6.0$ .

0.1542 „ 18.8 c.c. of nitrogen at  $16^{\circ}$  and 742 mm.  $\text{N} = 13.9$ .

$\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C} = 64.7$ ;  $\text{H} = 5.9$ ;  $\text{N} = 13.7$  per cent.

This substance is moderately soluble in cold and readily so in hot alcohol, and has strongly acid properties, since it dissolves readily in dilute ammonia or sodium carbonate.

1-Phenyl-2:4:4-trimethyl-3:5-pyrazolidone,  $\text{C}_6\text{H}_5 \cdot \text{N} \begin{matrix} \text{CO} - \text{CMe}_2 \\ \text{NMe} \cdot \text{CO} \end{matrix}$ .

This substance is produced when the alcoholic solution of phenyldimethylpyrazolidone is mixed with one molecular proportion of alcoholic soda and then heated with excess of methyl iodide at  $100^{\circ}$  in a tightly-stoppered bottle for about half an hour. On evaporating the product on the water-bath, a brown oil is obtained which crystallises after some hours. After washing with sodium carbonate solution to remove unchanged phenyldimethylpyrazolidone and then with water, the crystals were dissolved in light petroleum and the solution left to crystallise, when large, flat plates separated which, after recrystallisation from the same solvent, gave the following results on analysis:

0.1563 gave 0.3788  $\text{CO}_2$  and 0.0924  $\text{H}_2\text{O}$ .  $\text{C} = 66.1$ ;  $\text{H} = 6.5$ .

0.1466 „ 16.8 c.c. of nitrogen at  $18^{\circ}$  and 750 mm.  $\text{N} = 13.1$ .

$\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{C} = 66.1$ ;  $\text{H} = 6.4$ ;  $\text{N} = 12.8$  per cent.

Phenyltrimethylpyrazolidone melts at  $72^{\circ}$  and is readily soluble in benzene, alcohol, ether, and boiling light petroleum, but it is only sparingly soluble in the latter solvent in the cold.

When slowly crystallised, it forms large, transparent, six-sided prisms with well defined summits; when treated with hydriodic acid by Zeisel's method, no methyl iodide is formed.

\* The boiling must not be prolonged, as otherwise further decomposition takes place and the product is difficult to purify.

*Action of p-Bromophenylhydrazine on the Substance  $C_{14}H_{18}O_8N_2$ .*

Owing to the complicated nature of the substances produced by the action of phenylhydrazine, and in order that there might be no doubt as to their molecular weights and composition, an exactly similar series of experiments was carried out with *p*-bromophenylhydrazine. The results of these showed that, although the latter reacts less vigorously, it gives rise to a series of compounds analogous with those obtained by means of the former reagent. The proportions used were about 1 molecular proportion of  $C_{14}H_{18}O_8N_2$ , 2 of the hydrazine, and a little more than 1 of glacial acetic acid, the experiment being conducted in the following way.

The substance  $C_{14}H_{18}O_8N_2$  (7 grams), dissolved in 50 c.c. of warm alcohol, was cooled until it began to crystallise, and then a solution of *p*-bromophenylhydrazine (7 grams) and glacial acetic acid (3 c.c.) in 20 c.c. of alcohol was gradually added, the mixture being thoroughly cooled with water. In the course of a couple of hours, the orange-yellow solution had deposited a mass of stellate groups of bright orange crystals, which were collected and washed with alcohol, 4.4 grams of the substance being thus obtained :

0.4008 gave 0.1944 AgBr. Br = 20.64.

0.3625 „ 0.1748 AgBr. Br = 20.5.

0.1484 „ 0.2379  $CO_2$  and 0.0601  $H_2O$ . C = 43.7 ; H = 4.5.

0.1488 „ 18.5 c.c. of nitrogen at  $14^\circ$  and 758 mm. N = 14.5.

$C_{14}H_{15}O_4N_4Br$  requires C = 43.8 ; H = 3.9 ; Br = 20.8 ; N = 14.6 per cent.

This substance melts at about  $159^\circ$ , and, like the corresponding substance  $C_{14}H_{16}O_4N_4$ , obtained with the aid of phenylhydrazine, the melting point is lowered by recrystallisation from alcohol.

It dissolves in dilute aqueous caustic potash with a yellow colour, and if the solution is immediately acidified it is deposited unchanged ; a specimen thus treated gave Br = 20.7, whereas the unchanged substance contains 20.8 per cent. of bromine, but, left in contact with alkali, it decomposes.

*Methyl Bromophenylhydrazidimethylmalonate,*  
 $CO_2Me \cdot CMe_2 \cdot CO \cdot NH \cdot NH \cdot C_6H_4Br$ .

When the alcoholic mother liquors from the substance  $C_{14}H_{15}O_4N_4Br$  are allowed to evaporate spontaneously, they yield a crystalline product mixed with tarry matter, which, however, can be almost entirely removed by washing with ether. The residue, which contains traces of the orange-coloured compound,  $C_{14}H_{15}O_4N_4Br$ , is crystallised several



times from benzene, the crystals being always collected before that substance separates. Lastly, by crystallising two or three times from alcohol, the new compound is obtained quite colourless.

0.1502 gave 0.2492  $\text{CO}_2$  and 0.0671  $\text{H}_2\text{O}$ .  $\text{C} = 45.3$ ;  $\text{H} = 5.0$ .

0.4024 „ 0.2382 AgBr.  $\text{Br} = 25.2$ .

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$  requires  $\text{C} = 45.7$ ;  $\text{H} = 4.8$ ;  $\text{Br} = 25.4$  per cent.

*Methyl bromophenylhydrazidimethylmalonate* melts at  $96^\circ$ , and is very soluble in boiling alcohol or benzene, but rather sparingly so in the latter solvent in the cold.

*Action of Alkalis on the Compound  $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$  (p. 1227).*

The bright red compound  $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$  dissolves in caustic soda, forming a deep orange-red solution, and if this is at once acidified, a good deal of the substance is precipitated unchanged. The alkaline solution, however, soon becomes paler in colour, and commences to deposit a crystalline salt, excess of alkali hastening the separation, as the salt is sparingly soluble in strong alkaline solutions. The slimy mass of satiny plates is collected at the pump and washed with dilute caustic soda until the filtrate\* is no longer deep yellow; the buff-coloured residue is dissolved in hot water, acidified with hydrochloric acid, the precipitate washed and dissolved in boiling benzene, when, on cooling, the new substance separates in thin, buff-coloured scales which melt at  $163\text{--}164^\circ$ .

0.1515 gave 0.3201  $\text{CO}_2$  and 0.0643  $\text{H}_2\text{O}$ .  $\text{C} = 57.6$ ;  $\text{H} = 4.7$ .

0.1692 „ 29.6 c.c. of nitrogen at  $16^\circ$  and 759 mm.  $\text{N} = 20.4$ .

$\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_4$  requires  $\text{C} = 57.4$ ;  $\text{H} = 4.4$ ;  $\text{N} = 20.6$  per cent.

This acid is very sensitive to light and rapidly becomes brownish-yellow when exposed to sunlight. It dissolves readily in dilute ammonia and also in sodium carbonate solution, and, as it is insoluble in water, it could be directly titrated. The experiment showed that 1.4 grams required for solution 28 c.c. of normal sodium hydroxide, whereas a monobasic acid of the formula  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_4$  would neutralise 27.3 c.c.

The *calcium salt*. In preparing this salt, the solution of the acid in the exact amount of caustic soda was warmed, mixed with a few drops of calcium chloride, and well shaken. The precipitate was removed by filtration, excess of calcium chloride added to the filtrate, and the precipitated salt, which was gelatinous at first,

\* On acidifying, this filtrate deposits a small quantity of a scarlet, crystalline substance which has not been further investigated.

but soon appeared to become crystalline, was collected at the pump and washed with cold water. The salt, when dried over sulphuric acid *in vacuo*, becomes strongly electrical and difficult to handle.

0.5004 gave 0.1150  $\text{CaSO}_4$ .  $\text{Ca} = 6.7$ .

0.4184 „ 0.0954  $\text{CaSO}_4$ .  $\text{Ca} = 6.7$ .

$(\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_4)_2\text{Ca}$  requires  $\text{Ca} = 6.8$  per cent.

The *barium* salt was prepared in an exactly similar manner, and is a pale yellow, very insoluble, amorphous precipitate. In determining the carbon and hydrogen, the substance was mixed with potassium bichromate, which accounts for the hydrogen being somewhat high.

A separate determination of hydrogen was therefore made by burning the salt with copper oxide in the ordinary way, and gave  $\text{H} = 3.4$  per cent.

0.2971 gave 0.4866  $\text{CO}_2$  and 0.1094  $\text{H}_2\text{O}$ .  $\text{C} = 44.9$ ;  $\text{H} = 4.1$ .

0.3082 „ 0.1055  $\text{BaSO}_4$ .  $\text{Ba} = 20.1$ .

$(\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_4)_2\text{Ba}$  requires  $\text{C} = 45.8$ ;  $\text{H} = 3.3$ ;  $\text{Ba} = 20.2$  per cent.

The *methyl* ester. In preparing this derivative, the sodium salt of the acid was heated in a bottle with methyl iodide at  $100^\circ$  for half an hour, when the product contained a heavy oil which, on cooling, solidified to a mass of prismatic crystals. These were pressed, washed with methyl alcohol and dilute sodium carbonate, and crystallised from methyl alcohol, from which the methyl ester separated in oblique, almost colourless, crystals.

0.1826 gave 0.3942  $\text{CO}_2$  and 0.0821  $\text{H}_2\text{O}$ .  $\text{C} = 58.8$ ;  $\text{H} = 5.0$ .

0.2171 „ 36.4 c.c. of nitrogen at  $18^\circ$  and 752 mm.  $\text{N} = 19.2$ .

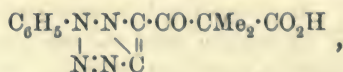
0.1641 „ 0.3530  $\text{CO}_2$  and 0.0760  $\text{H}_2\text{O}$ .  $\text{C} = 58.7$ ;  $\text{H} = 5.1$ .

0.1247 „ 20.9 c.c. of nitrogen at  $13^\circ$  and 754 mm.  $\text{N} = 19.6$ .

$\text{C}_{13}\text{H}_{11}\text{MeN}_4\text{O}_3$  requires  $\text{C} = 58.7$ ;  $\text{H} = 4.9$ ;  $\text{N} = 19.6$  per cent.

This methyl ester melts at  $88-89^\circ$  and is sparingly soluble in cold alcohol. It rapidly becomes yellow when exposed to light.

With regard to the constitution of the remarkable acid  $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_4$ , it is, as explained in the introduction, difficult to assign a satisfactory formula to it. The most probable expression seems to be



and the name suggested is *phenyltetrazinedimethylmalonylic acid*.





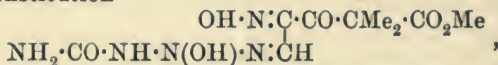
The solution gradually became pink, and a white, crystalline substance commenced to separate and slowly increased in quantity during several days. The precipitate was washed, first with alcohol and then with water, and afterwards extracted with boiling alcohol, in which it is very sparingly soluble. Two different preparations were analysed with the following results:

- 0.1627 gave 0.2209  $\text{CO}_2$  and 0.0798  $\text{H}_2\text{O}$ .  $\text{C} = 37.1$ ;  $\text{H} = 5.4$ .  
 0.1625 „ 32.6 c.c. of nitrogen at  $19^\circ$  and 769 mm.  $\text{N} = 23.3$ .  
 0.1791 „ 0.2415  $\text{CO}_2$  and 0.0834  $\text{H}_2\text{O}$ .  $\text{C} = 36.8$ ;  $\text{H} = 5.2$ .  
 0.1629 „ 33.9 c.c. of nitrogen at  $15^\circ$  and 750 mm.  $\text{N} = 24.1$ .  
 $\text{C}_9\text{H}_{15}\text{O}_6\text{N}_5$  requires  $\text{C} = 37.3$ ;  $\text{H} = 5.1$ ;  $\text{N} = 24.2$  per cent.

This substance melts at about  $170^\circ$  with rapid evolution of gas and the fused mass is dark brown in colour (see p. 1228).

It may be recrystallised from a large quantity of boiling alcohol, but appears to be decomposed to some extent during the operation. The specimen used in the first analysis had been recrystallised in this way. It dissolves in hot dilute hydrochloric acid, yielding a brown solution, and when it is heated with caustic potash it is decomposed with evolution of ammonia.

As explained in the introduction (p. 1228), this substance probably has the constitution



and is therefore *methyl semicarbaziglyoximedimethylmalonylate*.

*The Reduction of the Substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  by means of Tin and Hydrochloric Acid.*

In carrying out this reduction, the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  (10 grams) was dissolved in about 30 c.c. of alcohol, an excess of granulated tin was added, and then 15 c.c. of concentrated hydrochloric acid. On heating the mixture to the boiling point, very vigorous action set in, and continued without any further heating for a short time; this rapidly slackens, the operation being complete in about 5 minutes. The pale yellow solution was then decanted from the undissolved tin and allowed to cool, when it soon began to deposit crystals, and in the course of 24 hours became semi-solid. After several such operations had been made, the product was placed on a vacuum filter, the crystals washed, first with a little alcohol and then with water, and afterwards dried. The yield, from 10 grams of  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ , of this crystalline product, which may be called *A*, was usually 4 grams.

The filtrate from *A*, when diluted with a considerable quantity of water and allowed to remain for 24 hours, deposited a quantity of a white substance *B*.

After removing the tin by sulphuretted hydrogen, the filtrate was found to contain ammonium chloride, and, as it also reduced Fehling's solution in the cold, hydroxylamine was probably also present. The solution also contained a small quantity of some organic compound which became yellow on the addition of caustic alkali. The crystalline substance *A*, when dissolved in boiling alcohol and rapidly filtered, quickly deposited a quantity of flat, pale primrose-yellow needles, which, when very small, appear almost white. After two or three crystallisations, these were obtained pure and melted at  $177^{\circ}$ , the yield being about 18 per cent. of the  $C_{14}H_{18}O_8N_2$  employed. The formula of the substance *A* is  $C_{13}H_{16}O_5N_2$ .

The first alcoholic mother liquors, when concentrated, yielded a further small quantity of the same substance, and, after this had been filtered off and the filtrate evaporated to a small bulk, a white substance separated in slender needles.

When crystallised three or four times from alcohol, the purified product melts at about  $154^{\circ}$  with decomposition, but, if the heating is rapid, at  $157^{\circ}$ , or even slightly higher. This substance has the formula  $C_{14}H_{20}O_8N_2$ , and the yield obtained from 10 grams of  $C_{14}H_{18}O_8N_2$  was about 2.5 grams. The mother liquors contain small quantities of an isomeric compound (m. p.  $175-177^{\circ}$ ), but most of the latter is contained in the product *B*.

The latter was first freed from a little oily matter by extracting two or three times with boiling light petroleum, and then dried and dissolved in ether; the solution, when concentrated, slowly deposited slender needles, which were collected and crystallised a few times from ether. The substance then melted at  $154^{\circ}$ , and was found on examination to be identical with the above-mentioned compound  $C_{14}H_{20}O_8N_2$ . The ethereal mother liquors, when further concentrated, yielded small quantities of the same substance, and afterwards a mixture of this with the isomeride, melting at  $175-177^{\circ}$ . When this mixture was submitted to a number of fractional crystallisations, rejecting always the least soluble portions, the substance melting at  $175-177^{\circ}$  was ultimately obtained in a pure condition. It is much more soluble than the substance melting at  $154^{\circ}$ , and crystallises in hard masses which are not well defined, but generally consist of four-sided, oblique tables.

: Examination of the Substance  $C_{13}H_{16}O_5N_2$ , m. p.  $177^\circ$ .

0.1279 gave 0.2619  $CO_2$  and 0.0692  $H_2O$ . C = 55.8; H = 6.0.

0.1869 „ 0.3815  $CO_2$  „ 0.1013  $H_2O$ . C = 55.7; H = 6.0.

0.1268 „ 11.6 c.c. of nitrogen at  $15^\circ$  and 742 mm. N = 10.4.

0.1709 „ 15 c.c. „ „  $15^\circ$  „ 771 mm. N = 10.4.

$C_{13}H_{16}O_5N_2$  requires C = 55.7; H = 5.7; N = 10.1 per cent.

The name proposed for this substance is the *lactone of methyl glyazine-dihydrotetramethylidimalonylate* (see p. 1229), and in order to get some clue as to its constitution it was first examined for methoxyl groups by Zeisel's method.

0.3450 gave 0.2850 AgI. MeO = 10.9.

$C_{13}H_{16}O_5N_2$  containing one methoxyl group requires MeO = 11.1 per cent.

It was next found that it does not react with acetyl chloride and therefore does not contain hydroxyl groups.

The *semicarbazone*.—The substance  $C_{13}H_{16}O_5N_2$  (1 gram) was dissolved in boiling alcohol, mixed with a strong aqueous solution of semicarbazide hydrochloride (2 grams) and crystallised sodium acetate (2.5 grams), when the semicarbazone together with some sodium chloride soon crystallised out. After 24 hours, the liquid was decanted from the crystals, the latter were washed with a small quantity of alcohol, and then with water; this left the semicarbazone as a colourless, crystalline mass which weighed about 0.4 gram and melted at about  $230^\circ$ . A further small quantity was obtained by concentrating the alcoholic mother liquors.

0.1560 gave 0.2850  $CO_2$  and 0.0824  $H_2O$ . C = 49.8; H = 5.9.

0.1252 „ 22.2 c.c. of nitrogen at  $17^\circ$  and 752 mm. N = 20.4.

$C_{14}H_{18}O_5N_5$  requires C = 49.8; H = 5.6; N = 20.8 per cent.

The *oxime*. In preparing this substance, hydroxylamine sulphate (1 gram) was dissolved in a small amount of water to which sodium acetate was added together with sufficient alcohol to precipitate the bulk of the sodium sulphate. The filtered solution was added to the substance  $C_{13}H_{16}O_5N_2$  (1.4) dissolved in boiling alcohol.

On cooling, a little unchanged substance was deposited, and removed by filtration; the filtrate was concentrated to about one-third of its bulk, when four-sided crystals slowly separated. These were collected, washed with alcohol, and then with water, to remove any trace of sodium sulphate, and then again with alcohol. The oxime now melted at  $136^\circ$  and gave the following results on analysis:



0.1243 gave 0.2428  $\text{CO}_2$  and 0.0667  $\text{H}_2\text{O}$ .  $\text{C} = 53.3$ ;  $\text{H} = 5.9$ .

0.1492 „ 19 c.c. of nitrogen at  $17^\circ$  and 733 mm.  $\text{N} = 14.3$ .

$\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_2$  requires  $\text{C} = 52.9$ ;  $\text{H} = 5.7$ ;  $\text{N} = 14.3$  per cent.

*Action of phenylhydrazine.* When an alcoholic solution of phenylhydrazine and some acetic acid is added to a boiling alcoholic solution of the substance  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$ , the solution soon begins to deposit small, brilliant, prismatic crystals having a primrose-yellow colour, which are sparingly soluble in boiling alcohol and melt at  $270^\circ$ .

By using *p*-bromophenylhydrazine in the place of the phenylhydrazine, and conducting the operation in the same way, brilliant crystals similar to the above, but melting at  $196^\circ$ , are obtained.

These substances have not been further examined.

*Action of alkalis.* The substance  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$  dissolves in aqueous caustic potash with evolution of heat, yielding an orange-red solution which afterwards becomes somewhat paler. If this solution is warmed, it becomes yellow and then nearly colourless, and, when boiled, gives off ammonia and methyl alcohol. The acidified solution, on distillation, gives small quantities of hydrocyanic acid and a volatile fatty acid, which is probably isobutyric acid.

From the residue, a solid acid was obtained by extracting with ether, which, after purification by conversion into the zinc salt, melted at  $190^\circ$  and consisted of pure dimethylmalonic acid. The amount of this acid was considerable, being about 1 gram from 2.5 grams of the substance  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$ .

When the substance  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$  (in quantities of not more than 0.5 gram) is ground into a paste with water and then stirred with cold aqueous potash, it becomes orange-red and soon dissolves. If the mass is at once poured into dilute hydrochloric acid, a precipitate is produced, and after a few hours this is collected, washed with water, and dried. From alcohol, in which it is only moderately soluble, the substance separates in colourless needles, which, when heated in a capillary tube, become red and melt at  $214^\circ$  with decomposition.

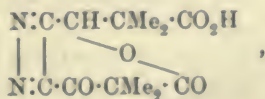
0.1696 gave 0.3373  $\text{CO}_2$  and 0.0835  $\text{H}_2\text{O}$ .  $\text{C} = 54.2$ ;  $\text{H} = 5.4$ .

0.1361 „ 0.2706  $\text{CO}_2$  „ 0.0662  $\text{H}_2\text{O}$ .  $\text{C} = 54.1$ ;  $\text{H} = 5.4$ .

0.2394 „ 22.4 c.c. of nitrogen at  $19^\circ$  and 752 mm.  $\text{N} = 10.6$ .

$\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$  requires  $\text{C} = 54.1$ ;  $\text{H} = 5.3$ ;  $\text{N} = 10.5$  per cent.

This substance is therefore the lactone of *glyazinedihydrotetramethyl-dimalonylic acid*,



produced from the methyl ester,  $C_{13}H_{16}O_5N_4$ , by simple hydrolysis. The barium salt,  $(C_{12}H_{13}O_5N_2)_2Ba$ , was prepared by boiling the acid with water and barium carbonate. The clear solution, on evaporating to a small bulk, deposited the salt as a crystalline mass, which was collected and dried, first over sulphuric acid and then at  $100^\circ$ .

0.2057 gave 0.0717  $BaSO_4$ .  $Ba = 20.5$ .

$(C_{12}H_{13}O_5N_2)_2Ba$  requires  $Ba = 20.5$  per cent.

This salt is rather soluble in water, and when the solution is acidified with hydrochloric acid, the acid separates and melts at  $214^\circ$ , showing that no change had taken place during the boiling with water and barium carbonate. When the acid is heated in a sealed tube with methyl alcohol and hydrochloric acid at  $100^\circ$ , it is converted into the methyl ester,  $C_{13}H_{16}O_5N_2$ , from which it had been obtained by hydrolysis.

When this methyl ester,  $C_{13}H_{16}O_5N_2$ , is ground with water and mixed with piperidine, it becomes orange-yellow, and partially dissolves with a slight rise of temperature. On heating on the water-bath, simple hydrolysis takes place, the solid soon disappears, and an orange-coloured solution is formed. Hydrochloric acid precipitates from this a copious, yellowish-white precipitate, which, when washed and dried, crystallises from alcohol in small, prismatic needles, melts at  $213^\circ$ , and consists of the lactone acid,  $C_{12}H_{14}O_5N_2$ .

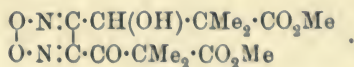
*Examination of the Substance  $C_{14}H_{20}O_8N_2$ , m. p.  $154^\circ$ .*

0.1710 gave 0.3076  $CO_2$  and 0.0924  $H_2O$ .  $C = 49.0$ ;  $H = 6.0$ .

0.1605 „ 11.6 c.c. of nitrogen at  $12^\circ$  and 765 mm.  $N = 8.6$ .

$C_{14}H_{20}O_8N_2$  requires  $C = 48.8$ ;  $H = 5.8$ ;  $N = 8.2$  per cent.

The name proposed for this substance is *methyl glyoximeperoxide-dihydrotetramethyldimalonylate*, and its constitution, which is discussed on p. 1230, is probably :



It is slightly soluble in water and has a very bitter taste. Like the substance  $C_{13}H_{16}O_5N_2$ , it dissolves in aqueous alkalis forming an orange-red solution, and, when boiled with caustic potash solution, decomposition sets in, and on acidifying and extracting with ether, dimethylmalonic acid is obtained.

The *semicarbazone* was prepared by mixing 3 grams of the substance dissolved in 5 c.c. of boiling alcohol with an aqueous solution

of 2 grams of semicarbazide hydrochloride and 2.5 grams of crystallised sodium acetate; small, prismatic crystals soon commenced to separate, and in about a week these had increased to a considerable extent. The substance, when washed with alcohol, then with water, and again with alcohol, was dried and analysed:

0.1698 gave 0.2771  $\text{CO}_2$  and 0.0914  $\text{H}_2\text{O}$ .  $\text{C} = 44.5$ ;  $\text{H} = 6.0$  per cent.

0.1381 „ 19.9 c.c. of nitrogen at  $16^\circ$  and 770 mm.  $\text{N} = 17.1$ .

$\text{C}_{13}\text{H}_{23}\text{O}_8\text{N}_5$  requires  $\text{C} = 44.9$ ;  $\text{H} = 5.7$ ;  $\text{N} = 17.4$  per cent.

The semicarbazone, prepared in this way, melts at about  $168-170^\circ$ ; it is sparingly soluble in cold alcohol, but may be crystallised from boiling alcohol, and is then obtained in groups of short crystals which melt at  $170-172^\circ$ .

When an alcoholic solution of the substance  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  (m. p.  $154^\circ$ ) is treated with phenylhydrazine and acetic acid, long, transparent, pale yellow crystals separate, which melt at  $205^\circ$ ; these, however, were not further investigated.

*Examination of the Substance  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$ , m. p.  $177^\circ$ .*

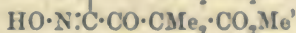
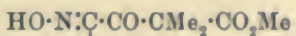
0.1555 gave 0.2785  $\text{CO}_2$  and 0.0820  $\text{H}_2\text{O}$ .  $\text{C} = 48.9$ ;  $\text{H} = 5.9$ .

0.1760 „ 12.8 c.c. of nitrogen at  $15^\circ$  and 770 mm.  $\text{N} = 8.2$ .

0.1982 „ 14.5 „ „ „  $20^\circ$  „ 762 mm.  $\text{N} = 8.4$ .

$\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  requires  $\text{C} = 48.8$ ;  $\text{H} = 5.8$ ;  $\text{N} = 8.6$  per cent.

This substance is evidently *methyl glyoximetetramethyldimalonylate*



and its constitution is discussed on p. 1230:

It is isomeric with, but differs widely in its properties from, the foregoing substance melting at  $154^\circ$  (p. 1260). Both, however, yield the substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  on oxidation with dilute nitric acid.

On treatment in the cold with strong caustic potash solution, it yields a plastic mass which, when rubbed, becomes a hard, yellow powder; this dissolves in water forming an orange-yellow, intensely bitter solution, and, on acidifying with hydrochloric acid, the original substance is reprecipitated. Boiling caustic potash solution decomposes the substance with formation of dimethylmalonic acid; it does not yield a semicarbazone.

The *diacetyl* compound. When boiled with acetic anhydride for a few minutes, the substance  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  (m. p.  $177^\circ$ ) dissolves, forming



a colourless solution and, after some hours, brilliant, colourless crystals separate. These were quickly recrystallised from alcohol and analysed :

0.1486 gave 0.2754  $\text{CO}_2$  and 0.0770  $\text{H}_2\text{O}$ .  $\text{C} = 50.6$  ;  $\text{H} = 5.7$ .

0.1991 „ 11.7 c.c. of nitrogen at  $18^\circ$  and 756 mm.  $\text{N} = 6.7$ .

$\text{C}_{14}\text{H}_{18}\text{N}_2(\text{C}_2\text{H}_3\text{O})_2\text{O}_8$  requires  $\text{C} = 50.4$  ;  $\text{H} = 5.6$  ;  $\text{N} = 6.5$  per cent.

This diacetyl compound, when boiled with alcohol, is slowly hydrolysed and, on cooling, crystals of the substance  $\text{C}_{14}\text{H}_{20}\text{O}_8\text{N}_2$  (m. p.  $175-177^\circ$ ) separate.

*Reduction of the Substance  $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$  with Zinc Dust and Acetic Acid.*

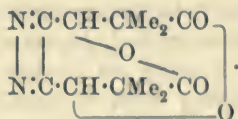
In carrying out this experiment, the substance was dissolved in glacial acetic acid at about  $40^\circ$ , and a considerable excess of zinc dust slowly added in small quantities. The solution immediately became deep yellow, but, as the temperature gradually rose to the boiling point, the colour almost entirely disappeared. On adding water, nothing separated, and, after filtering from the undissolved zinc, the solution was distilled in steam in order to remove as much acetic acid as possible. The residue in the distilling flask was concentrated considerably and allowed to remain overnight; the deep yellow crystals which had separated were then collected and washed with water. After repeated recrystallisation from methyl alcohol, in which the pure substance is very sparingly soluble, yellow, crystalline crusts were obtained which, on analysis, gave the following results :

0.1327 gave 0.2795  $\text{CO}_2$  and 0.0734  $\text{H}_2\text{O}$ .  $\text{C} = 57.5$  ;  $\text{H} = 6.0$ .

0.2244 „ 21.5 c.c. of nitrogen at  $15^\circ$  and 750 mm.  $\text{N} = 11.1$ .

$\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 57.6$  ;  $\text{H} = 5.6$  ;  $\text{N} = 11.2$  per cent.

As explained in the introduction, this substance is probably the dilactone of *glyazinetetrahydrotetramethyldimalonylic acid* (p. 1230) :



It softens at about  $255^\circ$  and melts at  $270-275^\circ$  with decomposition ; it dissolves readily in aqueous caustic alkalis, requiring for complete solution two molecular proportions of caustic soda. The dilactone does not dissolve in dilute ammonia or sodium carbonate solution in the cold,

and even on warming, dissolution takes place only slowly. During the combustion of the substance, it was noticed that a fluffy yellow sublimate formed on the tube, which subsequently melted and decomposed with great difficulty.

In conclusion, I wish to express my thanks to Messrs. Joseph Yates and D. Trevor Jones, of Owens College, for their valuable assistance in connection with the large amount of analytical work required by this research.

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## CXX.—*The Reaction between Phosphorus and Oxygen.* *Part I.*

By EDWARD JOHN RUSSELL.

It is well known that the rate of oxidation of phosphorus increases as the pressure of oxygen diminishes, and no satisfactory explanation of this apparent exception to the law of mass action has yet been given. A careful study of the reaction has been made, and several other anomalies have been found. This paper contains the results of the first part of the investigation.

### *Preparation of the Materials.*

(1) The phosphorus, which had been proved to be free from arsenic, was heated with phosphorus trichloride in a sealed tube at  $200^{\circ}$  for two days in order to decompose any hydride; the trichloride was then distilled off, the last traces being removed in a current of carbon dioxide. Another tube, with side tubes attached, was now sealed on to the reaction tube and the apparatus exhausted. Heat was applied, when the phosphorus distilled over and was collected in the side tubes, the pump being continuously in action so as to remove the small quantities of gas which are evolved. The tubes, which were quickly sealed off and kept in a dark place, now contained the phosphorus as a clear, highly refractive liquid, which after a time set to a white, waxy solid.

(2) The method of purifying the phosphoric oxide was that recommended by Shenstone and Beck (*Trans.*, 1893, 63, 475), the oxide being distilled in a stream of oxygen over red-hot spongy platinum until the product no longer reduced a solution of silver nitrate.

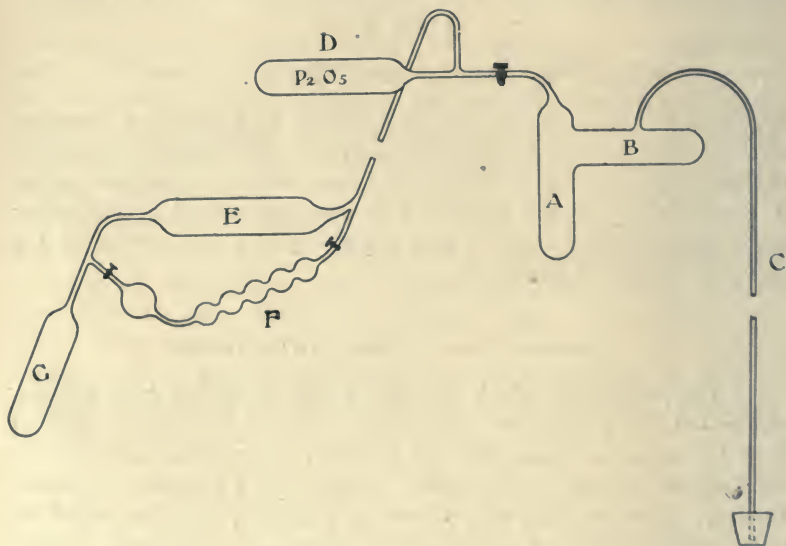
(3) The oxygen was obtained from recrystallised potassium chlorate which had been kept fused for some time to expel moisture. This was

transferred to a hard glass tube closed at one end, and the other end was then drawn out to form a delivery tube.

Duplicate experiments were sometimes made with oxygen obtained from potassium permanganate, but no difference in the results could be detected.

The apparatus (see Fig. 1) was thoroughly cleaned out with boiling concentrated nitric acid and dried at a high temperature. The end of the gauge *C* was dipped under mercury, and the whole exhausted by a Töppler pump. Purified phosphorus pentoxide was then distilled into *B* and *D* and phosphorus into *A*, the pump being meanwhile kept working. The supply tubes containing these two reagents were then

FIG. 1.



sealed off, and the apparatus left as shown in the sketch. After some months, when it was thought that drying was complete, the second part of the apparatus was sealed on through a T-piece afterwards joined to the pump. This was so arranged that the oxygen generated in *G* could, in the first series of experiments, pass through the phosphorus pentoxide in *E*, and in the second series through the sulphuric acid in *F* before reaching the phosphorus. The completed apparatus was exhausted, and left standing for a further period.

*First Series.*—*A* and *B* were surrounded by a bath of ice and salt, and oxygen introduced until the pressure was about 50 mm.; the temperature was raised to 15°, and the time required for absorption



was found to be about one hour. The amount of water present in oxygen, when dried in this way, is considered by Morley to be not more than 1 milligram in 40,000 litres (*Amer. J. Sci.*, 1887, 34, 200).

*Second Series.*—The oxygen, being dried by sulphuric acid, contains about 1 milligram in 400 litres (Morley, *loc. cit.*); the rate of absorption was very rapid, only 2 or 3 minutes being required.

*Third Series.*—Two similar tubes containing quantities of phosphorus with approximately equal surfaces were prepared (see Fig. 2) and filled with oxygen. In the one, sulphuric acid was present, and in the other, water. The dried phosphorus reacted much more quickly than the moist.

These experiments show that an increase in the amount of water increases the velocity of oxidation, but that a maximum is soon reached, after which further additions have a retarding influence. Many attempts were made to determine the limits within which the most favourable quantity of water lay, but with only partial success. The general result was that oxidation was most rapid when the phosphorus and oxygen had been dried over sulphuric acid, and the phenomena of oxidation in these circumstances were carefully observed.

#### *Substances formed during Oxidation.*

Schönbein (*Poggendorff's Annalen*, 1845, 65, 69; also *ibid.*, 169) and Schmidt (*J. pr. Chem.*, 1866, 98, 414) showed that unless water is present neither hydrogen peroxide nor ozone is produced. My experiments fully confirm this result. Phosphorus was distilled into an exhausted tube connected at either end with sulphuric acid drying bulbs; the apparatus was left to dry; oxygen was passed through and then treated with potassium iodide and starch solution. The experiment was repeated under pressures varying from 100 mm. to 760 mm., both with oxygen and air, but, although oxidation was rapid and the phosphorus glowed brightly, ozone could not be detected.

When moist oxygen was passed over the phosphorus, both ozone and hydrogen peroxide were formed in notable quantities.

The production of ozone during the oxidation of phosphorus, therefore, requires the intervention of a large amount of water, and does not take place in presence of the small quantity most favourable for the reaction of oxidation. The experiments dealt with in this part of the paper are therefore not complicated by the presence of ozone or hydrogen peroxide.

The oxides produced are white; red and yellow substances are only produced in the light or towards the end of the reaction when, as will afterwards be seen, the velocity of oxidation increases rapidly and the temperature rises.

*The Velocity of Oxidation.*

Ikeda (*Journ. Coll. Sci. Imperial Univ. Japan*, 1893, 6, 43) has studied the velocity of oxidation in moist air and found that it was proportional to the partial pressure of oxygen up to a certain point. Ewan, in a very interesting paper (*Phil. Mag.*, 1894, 38, 505), confirmed this result, and claimed to obtain a similar one for moist oxygen. In dry oxygen, however, the process appeared to be different; the velocity seemed to be proportional to the square root of the pressure of the gas. He supposed that the rate of oxidation was proportional also to the rate of evaporation of the phosphorus, and modified the usual equation by introducing Stefan's equation,  $v = c \cdot \log P / (P - p')$ , where  $v$ ,  $P$ ,  $p'$  are the rate of evaporation, total pressure, and vapour pressure of the evaporating substance respectively, whilst  $c$  is a constant. This expression was obtained by studying the rate at which ether evaporated in a tube, the end of which was open to the air. The equation therefore becomes:

$$-dp/dt = Kp \cdot \log P / (P - p'),$$

where  $p$  is the partial pressure of oxygen,  $P$  the total pressure due to oxygen, nitrogen, water vapour, and phosphorus vapour, and  $p'$  the partial pressure of the phosphorus vapour. This is easily integrated and gives:

$$Kt = \frac{P_0 - P}{p'} - \left( \log \frac{P_0 - a}{P - a} \right) \left( \frac{a}{p'} - \frac{1}{2} \right),$$

where  $P_0$  is the total pressure at the beginning of the reaction, and  $a$  the pressure of nitrogen, water, and phosphorus.

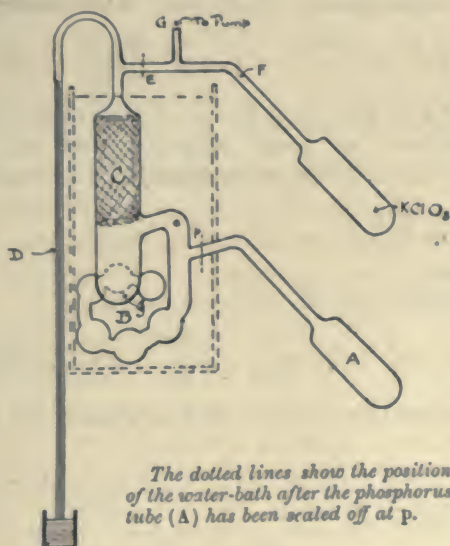
As indicated by Ewan's tables, the values of  $K$  appear to be fairly constant in the experiments with moist air, but this does not usually happen with moist oxygen; out of nine experiments, satisfactory results were obtained only in three cases. It cannot either be said that the results justify the expression given for oxidation in dry oxygen; the total fall of pressure was 200 mm., but only over the last 70 mm. do the results agree with the expression.

In Fig. 2 (p. 1267),  $C$  is a tube containing glass wool soaked in pure sulphuric acid, the excess of which can run to the bottom at  $g$ . Into this is sealed a wide tube,  $B$ , carrying some bulbs and also a wide tube,  $A$ , to hold the phosphorus.  $D$  is a mercury gauge,  $G$  is connected with a Töpler pump, and  $F$  with a Jena glass tube containing the potassium chlorate.

The apparatus having been exhausted,  $A$  is heated and pure phosphorus carefully distilled into  $B$ , the pump being again continually in action so as to remove the last traces of gas; finally  $A$  is sealed off.

The phosphorus collects in large drops all over *B*, a layer of liquid also lies in the bulbs. A large surface is essential to the success of the experiment. A tin bath is now placed round *B* and *C*, filled with a mixture of ice and salt, oxygen is generated, at first to wash out the apparatus and then to fill it under atmospheric pressure, the apparatus is then sealed off at *E*, being thus disconnected from the pump and the oxygen generator, finally the freezing mixture is displaced by water at a constant temperature. After two or three hours, readings of the pressure were taken by means of a cathetometer and a standard brass scale. The results are set out below in the first two columns; the numbers given in the columns  $K_1$ ,  $K_2$ , &c., are obtained by substituting

FIG. 2.



the experimental values in the four equations given below. Should any one of the equations represent the progress of the reaction, the numbers obtained would be constant.

Under the heading  $K_1$  are given the values calculated from the ordinary equation,

$$-dp/dt = K_1 p,$$

which, on integration, gives

$$K_1 = \frac{1}{t} \log \frac{P_0}{P} \quad \dots \dots \dots (1).$$

The values of  $K_2$  are calculated from the equation

$$-dp/dt = K_2 p^3;$$



on integration, this becomes

$$K_2 = \frac{1}{t} \cdot (P_0^{\frac{1}{2}} - P^{\frac{1}{2}}) \quad \dots \quad (2),$$

the rate of oxidation being supposed to be proportional to the square root of the pressure of oxygen, in accordance with Ewan's deduction.

For  $K_3$ , the equation

$$-dp/dt = K_3 p \log P/(P-p') \quad \dots \quad (3)$$

was used, and for  $K_4$  the equation

$$-dp/dt = K_4 p^{\frac{1}{2}} \log P/(P-p') \quad \dots \quad (4).$$

Equations (3) and (4) are derived from equations (1) and (2) by assuming that the rate of oxidation is also proportional to the rate of evaporation. The integration of (3) leads to the result:

$$K_3 t = \frac{P_0 - P}{p'} - \left( \log \frac{P_0 - a}{P - a} \right) \left( \frac{a}{p'} - \frac{1}{2} \right).$$

Now  $a = p'$ , and  $p'$  is very small compared with  $P$ , hence the first term  $(P_0 - P)/p'$  becomes so great compared with the second term  $\frac{1}{2} \log(P_0 - a)/(P - a)$  that this can be neglected, whereupon the equation becomes

$$K_3 t = P_0 - P \quad \dots \quad (5),$$

$p'$  being constant.

The integration of equation (4) gives the result

$$K_4 t = \frac{2}{3p'} \left[ (P_0 - a)^{\frac{3}{2}} - (P - a)^{\frac{3}{2}} \right] + \left( \frac{2a}{p'} - 1 \right) \left[ (P_0 - a)^{\frac{1}{2}} - (P - a)^{\frac{1}{2}} \right]$$

and since  $a = p'$  and  $(P_0^{\frac{1}{2}} - P^{\frac{1}{2}})$  is small compared with  $(P_0^{\frac{3}{2}} - P^{\frac{3}{2}})$ , this becomes

$$K_4 t = P_0^{\frac{3}{2}} - P^{\frac{3}{2}} \quad \dots \quad (6)$$

By differentiating (5) we get

$$dp/dt = K',$$

and by differentiating (6) we get

$$dp/dt = K'' p^{\frac{1}{2}},$$

or, in other words, the assumption that the velocity of reaction is proportional both to the pressure of oxygen and to the rate of evaporation of the phosphorus leads to the same result as the assumption that the velocity is altogether independent of the pressure of oxygen; whilst the hypothesis that the rate of oxidation is proportional both to the square root of the partial pressure of oxygen and to the rate of evaporation of the phosphorus leads to the same result as the assumption that the velocity is inversely proportional to the square root of the partial pressure of oxygen.

It should be noted that the values  $K_1$ ,  $K_2$ , &c., are not the absolute values, but only proportional to them. To obtain absolute values, a knowledge of the active mass of the phosphorus would be required, a determination which would be difficult, if not impossible, to carry out, and which seems to be unnecessary, for so long as the surface is sufficiently great the active mass can be assumed to be constant in any given experiment, although the values of  $K$ , &c., obtained in different experiments cannot be compared.

*Expt. 1.  $t = 18.6^\circ$ .*

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | $K_2$ . | $K_3$ . | $K_4$ . |
|----------------|---------------------------|---------|---------|---------|---------|
| 0              | 669.82                    | —       | —       | —       | —       |
| 0.75           | 638.24                    | 279     | 82.4    | 421     | 162     |
| 3.00           | 527.49                    | 346     | 97.1    | 474     | 174     |
| 3.50           | 497.99                    | 368     | 102     | 490     | 178     |
| 4.00           | 468.20                    | 389     | 106     | 504     | 180     |
| 5.08           | 395.12                    | 451     | 118     | 540     | 187     |
| 6.25           | 295.35                    | 569     | 139     | 599     | 196     |
| 6.75           | 236.05                    | 671     | 156     | 642     | 203     |
| 7.00           | 200.42                    | 749     | 167     | 671     | 207     |
| 7.25           | 163.14                    | 846     | 181     | 699     | 210     |
| 7.53           | 106.87                    | 1058    | 206     | 747     | 215     |
| 8.08           | nil                       | 1068    | 335     | 866     | 224     |

(See Curve 1, p. 1270.)

*Expt. 2.  $t = 13.8^\circ$ .*

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | $K_2$ . | $K_3$ . | $K_4$ . |
|----------------|---------------------------|---------|---------|---------|---------|
| 0              | 342.54                    | —       | —       | —       | —       |
| 3.00           | 328.74                    | 816     | 172     | 92      | 167     |
| 4.75           | 308.94                    | 944     | 196     | 103     | 167     |
| 5.75           | 298.18                    | 1047    | 215     | 113     | 202     |
| 6.75           | 287.55                    | 1126    | 230     | 119     | 212     |
| 7.75           | 277.35                    | 1183    | 239     | 126     | 217     |
| 8.00           | 274.14                    | 1209    | 244     | 125     | 220     |
| 8.25           | 272.01                    | 1214    | 244     | 125     | 220     |
| 18.5           | 80.66                     | 3395    | 515     | 211     | 301     |
| 20             | nil                       | —       | 925     | 281     | 322     |

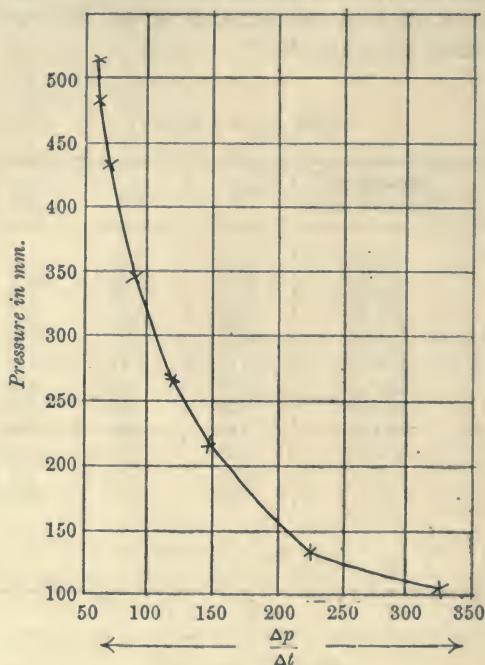
In each case, the absorption began at 770 mm. pressure, but the earlier readings were not taken.

Experiments tried at a higher temperature ( $25^\circ$ ) failed because the

phosphorus caught fire when the pressure had fallen to about 500 mm.

Experiments were next made in which calcium chloride replaced sulphuric acid as the drying agent.

CURVE 1.



*Expt. 3.  $t = 16.6^\circ$ .*

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | $K_2$ . | $K_3$ . | $K_4$ . |
|----------------|---------------------------|---------|---------|---------|---------|
| 0              | 534.55                    | —       | —       | —       | —       |
| 1.00           | 486.00                    | 414     | 107     | 485     | 165     |
| 2.00           | 436.73                    | 439     | 111     | 489     | 162     |
| 3.50           | 358.87                    | 494     | 119     | 502     | 156     |
| 4.00           | 332.52                    | 515     | 122     | 505     | 157     |
| 4.50           | 303.80                    | 543     | 126     | 513     | 157     |
| 5.00           | 272.82                    | 584     | 132     | 523     | 157     |
| 5.50           | 238.59                    | 637     | 139     | 502     | 157     |
| 6.00           | 198.59                    | 717     | 150     | 560     | 159     |
| 6.50           | 149.03                    | 853     | 168     | 593     | 162     |
| 6.75           | 119.93                    | 962     | 180     | 614     | 164     |
| 7.00           | 84.85                     | 1142    | 198     | 642     | 165     |
| 7.15           | 81.40                     | 3232    | 245     | 704     | 170     |
| 7.20           | nil                       | 10113   | 321     | 742     | 172     |



Expt. 4.  $t = 19.6 - 19.8^\circ$ .

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | $K_2$ . | $K_3$ . | $K_4$ . |
|----------------|---------------------------|---------|---------|---------|---------|
| 0              | 666.40                    | —       | —       | —       | —       |
| 0.50           | 644.37                    | 277     | 422     | 440     | 169     |
| 1.00           | 624.52                    | 276     | 417     | 416     | 158     |
| 1.50           | 606.21                    | 274     | 411     | 401     | 152     |
| 2.00           | 587.78                    | 273     | 406     | 393     | 148     |
| 3.00           | 554.00                    | 270     | 396     | 375     | 139     |
| 4.25           | 515.44                    | 266     | 384     | 355     | 129     |
| 5.50           | 479.96                    | 263     | 373     | 339     | 121     |
| 7.00           | 437.10                    | 264     | 366     | 326     | 115     |
| 16.00          | 134.27                    | 417     | 442     | 332     | 76.8    |
| 16.75          | 87.41                     | 500     | 484     | 345     | 97.8    |
| 17.00          | 65.07                     | 427*    | 428*    | 694*    | 764*    |
| 17.08          | 56.54                     | 473     | 457     | 719     | 768     |
| 17.16          | 46.79                     | 543     | 502     | 756     | 780     |
| 17.25          | 34.76                     | 667     | 576     | 816     | 800     |
| 17.33          | 18.53                     | 962     | 706     | 915     | 826     |
| 17.41          | nil                       | 2427    | 1169    | 1010    | 800     |

(See Curve 2, p. 1272.)

\* Oxidation being now very rapid, these and the following numbers indicate the progress of the reaction after 16.75 hours.

In the curves, the values of  $dp/dt$  have been plotted as ordinates, and the values of  $p$  as abscissæ.  $dp/dt$  evidently increases considerably as  $p$  diminishes. With the wide variations in the values obtained for  $K_1$ ,  $K_2$ , &c., it is clear that none of the equations hold, therefore we are not justified in supposing that the rate of oxidation is proportional either to the square root of the partial pressure of oxygen or to the partial pressure. In experiment 4, readings were taken at pressures higher than 500 mm., and it will be noticed that  $dp/dt$  diminishes with  $p$  as far as 480 mm., after which it increases. And a glance at the figures given under  $K_1$  show that this fall in the velocity is directly proportional to the fall in pressure. This result suggests that the reaction between phosphorus and oxygen can be divided into two stages; in the first, the velocity is directly proportional to the pressure, and in the second it increases as the pressure diminishes, but not in any simple ratio.

#### *Oxygen under High Pressure.*

In this series of experiments, the initial pressure of the oxygen was between two and three atmospheres. The apparatus was somewhat modified by bending the gauge upwards to a height of three metres;

the tube leading to the pump was sealed off as soon as the last exhaustion was finished, but the oxygen generator had to be left on. Water-jackets were arranged round all parts of the apparatus out of the bath. The results are given in the following tables (p. 1273); in only one

case was the reaction continued until all the oxygen was absorbed, in the others, it was interrupted so as to determine which oxide was produced.

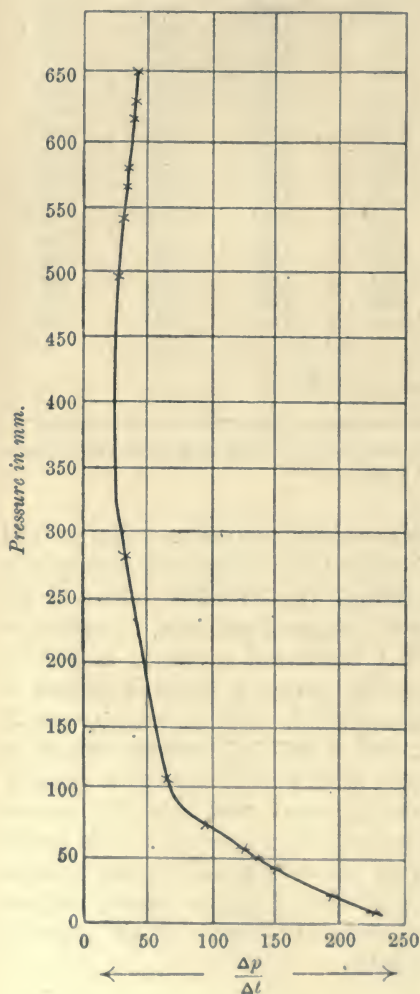
Similar results were obtained in both series of experiments when the oxygen was generated from potassium permanganate.

Owing to the disposition of the apparatus it was not possible to use the cathetometer, and readings had to be taken on a scale fixed to the gauge; the readings are therefore not so accurate as those of the first series. The results lead us to two remarkable conclusions. In the first place, they contradict the usual statement that phosphorus only reacts with oxygen under low pressures; the initial pressure of oxygen in experiment 2 was 2000 mm. In the second place, as  $K_1$ , calculated from equation (1), p. 1267, is now constant, it follows that the velocity of this reaction is proportional to the pressure of oxygen, and therefore down to a certain pressure the reaction is unimolecular.

During this first stage, there is phosphorescence, but it is so feeble that it is only seen after

the eye has become accustomed to darkness. In the second stage (the more rapid period), ordinary phosphorescence appears and there is no possibility of confusing the two glows. Doubtless this very feeble glow accounts for the first stage having been previously overlooked,

CURVE 2.



Expt. 1.  $t = 14-15.0^{\circ}$ .

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | Time in hours. | Pressure of oxygen in mm. | $K_1$ . |
|----------------|---------------------------|---------|----------------|---------------------------|---------|
| 0              | 1319.2                    | —       | 18             | 774.5                     | 128     |
| 1              | 1273.7                    | 156     | 20             | 730.0                     | 128     |
| 2              | 1231.6                    | 146     | 21             | 708.4                     | 128     |
| 6              | 1103.0                    | 129     | 22             | 687.4                     | 129     |
| 10             | 975.8                     | 131     | 24             | 639.3                     | 131     |
| 14             | 874.5                     | 127     | 25             | 615.3                     | 132     |

Expt. 2.  $t = 13-14^{\circ}$ .

| Time in hours. | Pressure of oxygen in mm. | $K_1$ . | Time in hours. | Pressure of oxygen in mm. | $K_1$ . |
|----------------|---------------------------|---------|----------------|---------------------------|---------|
| 0              | 1949.2                    | —       | 28.0           | 1513.2                    | 392     |
| 4.09           | 1887.3                    | 342     | 31.5           | 1468.4                    | 390     |
| 9.00           | 1809.3                    | 358     | 36.0           | 1410.1                    | 390     |
| 14.10          | 1723.1                    | 370     | 38.0           | 1392.3                    | 385     |
| 18.00          | 1663.6                    | 382     | 40.0           | 1368.5                    | 384     |
| 20.10          | 1629.7                    | 386     | 42.0           | 1345.0                    | 384     |
| 22.00          | 1602.0                    | 386     | 44.0           | 1324.7                    | 384     |
| 24.00          | 1573.9                    | 387     | 46.0           | 1301.5                    | 382     |
| 26.00          | 1544.8                    | 388     |                |                           |         |

for it is generally assumed that oxidation ceases as soon as the ordinary and relatively bright glow stops. Moreover, it is an essential condition to success that the surface of the phosphorus shall be quite clean, and one can only rely on fulfilling this condition by redistilling the phosphorus *in vacuo*, as was done in these experiments.

Phosphorus is extraordinarily sensitive to surface contamination, which either greatly retards oxidation or altogether stops it.\* On one occasion, the distillation had not gone quite smoothly and a certain amount of the liquid portion boiled over into the bulb. When oxygen was let in under 1900 mm. pressure, there was a slight action at first, the pressure falling about 60 mm., then the action stopped altogether and did not start again even when the temperature was

\* John Davy (*Edin. New Philos. Journ.*, 1833, 15, 48) found that when phosphorus was kept in oxygen under the atmospheric pressure for several hours, the volume was not much diminished, and Müller (*Ber.*, 1870, 3, 84) sealed up phosphorus with oxygen in a flask, left it for  $2\frac{1}{2}$  months, and then opened under water and found no change in volume. In both cases, there was no doubt a protective film on the surface.



raised to  $26^{\circ}$ . The apparatus was opened for a moment to let out the excess of oxygen, and then sealed up and more oxygen generated until the pressure was restored to 1900 mm.; this time the action was normal. Probably the sudden release of the pressure altered the surface of the phosphorus sufficiently to allow the oxidation to proceed.

*Preliminary Examination of the Oxide formed during the First Stage.*

This oxide is perfectly white, there being no buff-coloured substance produced here as in the next stage. When heated *in vacuo*, a few white crystals sublime, the rest of the substance breaking up into a white, crystalline sublimate, less volatile than the first, and a red residue. Finally, this red residue largely disappears, being apparently changed to ordinary phosphorus when heated for a longer time. The white, crystalline sublimate seems to be phosphorus tetroxide, and the red residue, amorphous phosphorus. On treating with water, the oxide only slowly dissolves; the solution reduces mercuric chloride and silver nitrate and gives a white precipitate with magnesia mixture, which, when examined under the microscope, is seen to differ altogether in crystalline form from the precipitate obtained with either of the three phosphoric acids, and is apparently identical with that obtained from a solution of phosphorous oxide. But the oxide does not melt on heating, whereas if it were phosphorous oxide, as the above reactions indicate, it should melt at  $22^{\circ}$ . I hope shortly to be able to determine the precise nature of the substance.

*Discussion of the Results. First Stage.*—The reaction being unimolecular, the first action would naturally be  $P_4 + O_2 = P_4O_2$ , and no doubt this oxide may have a transient existence. A little reflection will make it evident, however, that the reaction will still appear unimolecular if the  $P_4O_2$  is oxidised at an infinite velocity to  $P_4O_4$ , and this also at an infinite velocity to a higher oxide. If one of the two latter velocities is not infinite, but only somewhat greater than the first velocity, it ought to be possible to isolate the intermediate oxide, since this would not be oxidised quite so fast as it was produced, but only some short time afterwards.

Walker (*Proc. Roy. Soc. Edin.*, 1898, 22, 22) draws attention to Harcourt and Esson's investigation of two unimolecular reactions proceeding simultaneously. A substance  $A$  is transformed into  $C$  through an intermediate compound  $B$ ; if at a time  $t$ ,  $x$  is untransformed,  $y$  is in the intermediate state, and  $z$  in the final state, then  $x + y + z = A$ . Suppose the velocity constant  $A \rightarrow B$  be  $m$ , and  $B \rightarrow C$  be  $n$ , then at time  $t$  the rate of diminution of  $x$  is given by the equation  $-dx/dt$

$=mx$ , and the rate of increase of  $z$  by  $dy/dt=ny$ : it can then be shown that

$$z = A \left\{ 1 + \frac{n}{m-n} \cdot e^{-mt} + \frac{m}{n-m} \cdot e^{-nt} \right\} \quad (7).$$

In the special case when one of the coefficients,  $n$  for example, becomes infinitely great, this expression reduces to  $z = A(1 - e^{-mt})$ , the ordinary equation for a unimolecular reaction. Walker calculates values for  $z$  in his hypothetical reaction, assigning different values to  $m$  and  $n$ , and shows that the "constant"  $K$ , as calculated on the assumption that the reaction is single and unimolecular, would increase in value, rather rapidly at first, more slowly afterwards. Now the approximately constant values obtained for  $K$  seem to indicate that all the reactions but one proceed at so great a velocity that there is no prospect of isolating the other intermediate oxides which may be supposed to be formed.

It is, of course, quite possible that the constancy of  $K$  is only accidental, as is the case with an apparent constant discussed in the sequel (p. 1282).

*Second Stage.*—The intermediate oxide, whatever it is, obtained during the first stage evidently oxidises during the second stage, since the final product is phosphoric oxide. With this change proceeding at a finite velocity, the total action will be expressed by an equation which, at its simplest, will be of the form of equation 7, but probably will be more complex. It is not surprising, then, that no simple law could be discovered underlying the results at low pressures. Moreover, since the velocity tends to increase as the pressure diminishes with the progress of the reaction, it is hardly possible to assume that the system remains strictly isothermal, and no doubt the very rapid final rates in experiments 1 to 4 (pp. 1269, 1270, 1271) are due to a rise in temperature. This would also explain the presence, in the oxide obtained, of a small quantity of a buff-coloured substance, apparently amorphous phosphorus.

### *Influence of an Inert Diluting Gas.*

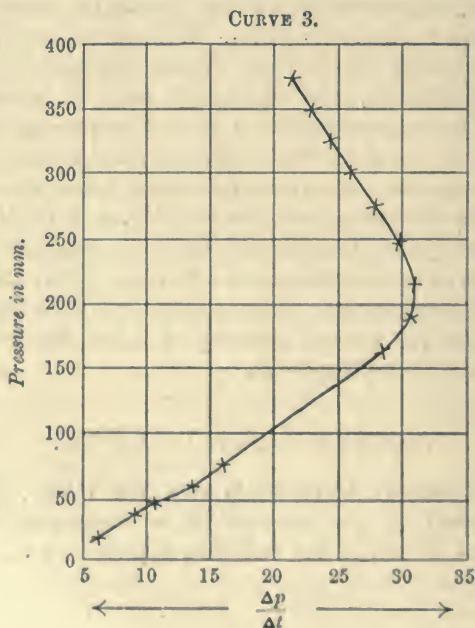
As it was necessary to ascertain how the velocity of oxidation would be affected by the presence of an inert gas, nitrogen was introduced as a diluent in the following experiments:

| <i>Expt. 1.</i>  |                           | <i>Expt. 2.</i>  |                           |
|--|---------------------------|--|---------------------------|
| Pressure of nitrogen = 165.2 mm.<br>$t = 19.2^{\circ}$ . |                           | Pressure of nitrogen = 240 mm.<br>$t = 13.6^{\circ}$ . |                           |
| Time in minutes.   | Pressure of oxygen in mm. | Time in minutes.                                       | Pressure of oxygen in mm. |
| 0  | 300.93                    | 0  | 393.42                    |
| 295  | 194.99                    | 45   | 327.14                    |
| 365  | 165.61                    | 90   | 247.54                    |
| 440  | 132.93                    | 135  | 160.05                    |
| 515  | 99.48                     | 180  | 91.93                     |
| 590  | 68.79                     | 225  | 46.93                     |
| 635  | 56.31                     | 270  | 19.38                     |
| 695  | 44.27                     | 315  | 6.30                      |
| 725  | 39.66                     |  |                           |

(See Curve 3).

Sulphuric acid was used as drying agent.

The curve given is that for experiment 2; the other is precisely



similar in form, but the turning point is at an oxygen pressure of about 120 mm. In experiment 2, the curve turns at 216 mm.; in a



third experiment, the pressure of the nitrogen was 56 mm. and the curve began to turn when the oxygen pressure had fallen to about 20 mm. ; the return always seems to begin when the oxygen pressure has fallen somewhat below the nitrogen pressure. Instead of increasing continuously to the end, the velocity reaches a maximum and then diminishes fairly rapidly.

This result is not difficult to understand. If a tube filled with air contains some phosphorus at the bottom, the oxygen in the lower layers of the air will be absorbed and there will be a steady drift of oxygen down the tube. This drift is, however, retarded by the nitrogen, and the retarding effect becomes greater as the pressure of the oxygen becomes less: in other words, the rate of oxidation diminishes as the partial pressure diminishes, because the oxygen has a greater difficulty in reaching the phosphorus. At a certain point, the retarding effect of the nitrogen more than counterbalances the acceleration connected with a fall in the partial pressure of oxygen, and from this point onwards the whole velocity diminishes.

The oxide formed is white, and the absence of any buff-coloured substance is no doubt connected with the fact that the action never proceeds very rapidly.

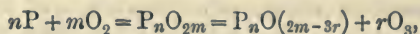
#### THE OXIDATION OF MOIST PHOSPHORUS.

This is the most commonly occurring case of the oxidation of phosphorus, and the more striking facts in connection with it have been known for a long time. There are some notable differences between this and the preceding case. Action only begins when the pressure is reduced below a certain amount, and ozone and hydrogen peroxide are invariably produced; if nitrogen is present, ammonium nitrate and nitrite are formed as well. Recently, certain emanations from moist oxidising phosphorus have been discovered; whether these are due to the special physical properties of the cloud formed by the oxidation products or whether they are definite rays coming from the phosphorus itself is not settled. Harm and also Elster and Geitel (*Phys. Zeit.*, 1903, 16, 457) incline to the latter opinion, Schmidt (*Ann. Phys.*, 1902, 10, 704) to the former. Phosphorus, as dried in the foregoing experiments, does not seem to have been the subject of any investigations of this kind.

#### *Side Reactions.*

*Ozone and Hydrogen Peroxide.*—Schönbein and Schmidt (*loc. cit.*) proved the presence of these substances among the oxidation products, and this has been confirmed by later workers (Leeds, *Chem. News*, 1879,

40, 70; and Wenzell, *Pharm. J.*, 1883, [iii], 14, 24). Kingzett, indeed (Trans., 1880, 37, 792), claimed to have found a regular connection between the amounts of hydrogen peroxide and ozone, but the difficulty of analysing the mixture must have been considerable. McLeod could not obtain any regular results (Trans., 1880, 37, 118). The substances are usually accounted for by supposing that during oxidation some oxygen molecules are dissociated and the oxygen atoms form ozone and hydrogen peroxide. Ostwald (*Zeit. Phys. Chem.*, 1900, 34, 248) gives some theoretical objections to this view, the general nature of which is that ozone, having a higher oxidation potential than the oxygen from which it was formed, can only be produced by the addition of energy. But the chemical energy of one reaction is not available for another and totally different reaction, and so the energy degraded during the oxidation of phosphorus cannot be utilised for producing ozone. He assumes that a higher peroxide must first be formed, subsequently breaking up into ozone and the stable oxide actually produced, and represents the reaction:



thus bringing the action into line with the work done by Bach, Engler, and Wild on autoxidation. Now Boche (*Ber.*, 1873, 6, 439) states that the oxidation of phosphorus gives rise to an oxide which generates hydrogen peroxide in contact with water. If this were so, it would be strong evidence in favour of Ostwald's theory and would account for all my observations, but I cannot find any evidence of such a substance.

Doubts have sometimes been raised as to whether the so-called ozone is really ozone or not. I find it possesses the following properties: (1) it passes, without condensation, through a tube 18 inches long cooled with solid carbon dioxide, (2) it rapidly destroys india-rubber, (3) it acts on mercury precisely as ozone does.

There seems to be little doubt that it is actually ozone.

*Ammonium Nitrite and Nitrate.*—I find that both of these are present, although only in small amount.\* The greatest care was taken to exclude ammonia, and it is difficult to account for their formation; the case does not stand quite by itself, however, for Norman Smith and I have found them in the products of oxidation of zinc and iron in moist air. Hydrogen peroxide is also formed, and the only differences between the oxidation of the metals and that of phosphorus are the production of ozone and the velocity of reaction.

\* So small as not to vitiate Lindemann's method of analysing air by means of phosphorus (*Zeit. Anal. Chem.*, 1879, 18, 158).



*Velocity of Oxidation.*

These experiments were carried out in the same way as the corresponding experiments with dry oxygen, the only difference being that water was substituted for sulphuric acid in the tube *C*.

*Experiments under High Pressures.*—As a rule, no reaction took place even after six months. In a few cases, reaction began but soon stopped, and the phosphorus became coated with a white substance which neither deliquesced nor showed any sign of change even after prolonged contact with the moist oxygen. But when the temperature was raised, ignition took place. This oxide is being investigated.

The cessation of action between phosphorus and moist oxygen when the pressure exceeds a certain amount is often quoted as an instance of false equilibrium. It was noticed in the experiments on dry phosphorus that reaction does not cease if the system is fairly dry; all the phenomena are, however, consistent with the idea of false equilibrium. Duhem supposes that there is a resistance to the reaction, and likens the system to a rough inclined plane bearing a weight at the end which is gradually being raised. If there were no friction, the weight should begin to move directly the end is lifted, but, as a matter of fact, the plane has to be inclined at a certain angle before any motion begins. He considers that this unexpected equilibrium is analogous to false equilibrium in chemical reactions. In the present instance, water vapour is the retarding agent. It is unfortunate that the velocity of oxidation of dried phosphorus cannot be represented by any simple expression, for it would not be difficult to put in a factor to stand for the friction effect. Some connection might then be traced between the amount of water vapour present and the pressure at which the reaction begins.

The curve (p. 1280) shows a retarding effect at work in the early part of the oxidation, followed by the rapid increase in velocity noted in the experiments with dry oxygen. When oxidation first begins, the luminosity is seen in only one or two places on the phosphorus, and not until nearly the end does the whole mass glow.

In trying to interpret these observations, the following possibilities have been considered: (a) a possible chemical action of water vapour on phosphorus. (b) A possible physical action of water vapour in modifying or protecting the surface of phosphorus. (c) The dynamical effect of an inert diluting gas.

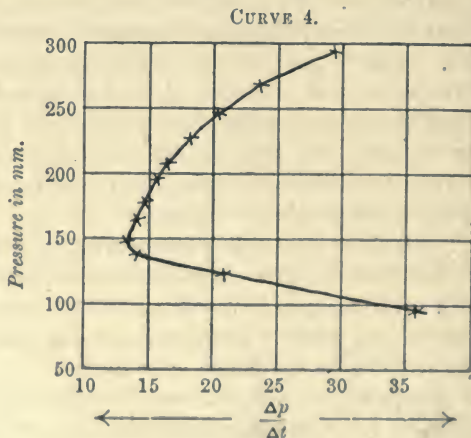
(a) *A Possible Chemical Reaction.*—Some phosphorus was distilled into an exhausted apparatus containing water as in the previous experiments, the apparatus sealed off and left in a warm place (18°) in the dark for two months, the gauge being read daily. There was no increase of



*Experiments under Low Pressures.*

| <i>Expt. 1.</i>   |                     | <i>Expt. 2.</i>   |                     |
|---|---------------------|---|---------------------|
| $t = 19-19.1^{\circ}$ . Pressure of aqueous vapour, 16.35 mm. |                     | $t = 23^{\circ}$ . Pressure of aqueous vapour, 20.9 mm. |                     |
| Time in minutes.  | Pressure of oxygen. | Time in minutes.  | Pressure of oxygen. |
| 0   | 335.62              | 0   | 327.14              |
| 30  | 281.51              | 10  | 294.40              |
| 60  | 250.07              | 20  | 268.74              |
| 90  | 225.28              | 30  | 246.62              |
| 120   | 203.77              | 40  | 227.00              |
| 150   | 184.72              | 50  | 209.64              |
| 275   | 109.15              | 60  | 193.40              |
| 305   | 92.25               | 70  | 178.07              |
| 365   | 53.93               | 80  | 163.18              |
| 395   | 32.57               | 90  | 149.38              |
| 425   | 8.85                | 100   | 136.39              |
| 440   | nil                 | 110   | 121.15              |
|   |                     | 120   | 94.29               |
|   |                     | 130   | 50.35               |
|   |                     | 140   | nil                 |

(See Curve 4.)



pressure and therefore no gas was formed. At the end of the time, the surface of the phosphorus was carefully examined, but no change in appearance could be detected.

Without further evidence, we do not seem justified in assuming that any chemical action takes place.

(b) *A Possible Physical Action.*—The part of the apparatus containing

the phosphorus was then surrounded by a freezing mixture, air was admitted, the water tube cut off, and a calcium chloride tube put into its place. The air was exhausted and oxygen passed in until the atmospheric pressure was attained. Inasmuch as the water was now removed and dry oxygen was present, oxidation should have gone on just as in the earlier experiments if the phosphorus had been unaltered by contact with the water vapour, but as a matter of fact no oxidation took place under this pressure until some months had elapsed. Water vapour does, therefore, in some way form a protecting film on the phosphorus surface.

(c) *The Effect of an Inert Gas.*—This does not seem to be great until almost the end of the reaction, and if 56 mm. of nitrogen only altered the curve near its end-point, it is doubtful whether 20 mm. of water would do more.

There is, of course, always the possibility that in presence of water vapour there may be a complete change in the mode of oxidation and that these results cannot be correlated with those on p. 1269. My experiments, however, do not favour this idea. If instead of 20 mm. pressure of water vapour only 4 mm. are employed, the velocity curve does not differ sensibly from those obtained for dry oxidations.

Two experiments are given, in which dilute sulphuric acid (44 per cent.) replaced the water in the apparatus.

| <i>Expt. 1.</i>  |                     | <i>Expt. 2.</i>  |                     |
|--|---------------------|--|---------------------|
| $t = 9^{\circ}$ . Tension of aqueous vapour,<br>4.2 mm.* |                     | $t = 11^{\circ}$ . Tension of aqueous<br>vapour, 4.6 mm. |                     |
| Time in minutes.   | Pressure of oxygen. | Time in minutes.   | Pressure of oxygen. |
| 0  | 467.27              | 0  | 464.63              |
| 15   | 424.97              | 30   | 429.80              |
| 30   | 381.68              | 60   | 389.53              |
| 45   | 332.64              | 90   | 348.44              |
| 60   | 276.65              | 120  | 300.43              |
| 75   | 209.67              | 150  | 248.32              |
| 90   | 112.83              | 180  | 185.47              |
| 97   | nil                 | 210  | 97.60               |
|  |                     | 225  | nil                 |
| (See Curve 5, p. 1282.)                                  |                     |  |                     |

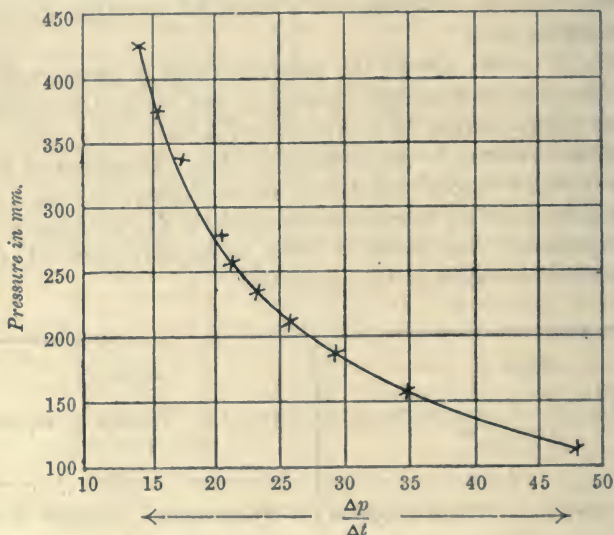
\* Sorel, *J. Soc. Chem. Ind.*, 1890, 9, 175.

In experiment 2, the apparatus was filled to a pressure of 760 mm., in experiment 1 to 520 mm. only.

Moreover, if oxygen fully saturated with water vapour is used, but the experiment conducted in such a way that water vapour has not had access to the phosphorus for any great length of time before oxidation begins, the curve again resembles those obtained with dried gases.

The modifying effect of water vapour can, I think, be explained entirely by the surface protection noted under (b). This would, in the first instance, tend to prevent oxidation; when it does start, it is at some point where the protection is weak, consequently oxidation is at first purely local. As the pressure diminishes, the velocity

CURVE 5.



increases, and the heat developed causes the reaction to spread until finally the whole mass of phosphorus is being acted on.

The appearance of the glow supports this view, which is also in accordance with the fact that the retarding effect is greatest during the earlier part of the oxidation.

Ewan and Ikeda both state that when moisture is present the velocity of oxidation in mixtures containing nitrogen is proportional to the partial pressure of oxygen, which, according to Ewan, is not the case when moisture is absent. This would suggest that the process of oxidation is different in the two cases of presence and absence of moisture. However, water vapour retards oxidation at the beginning, and nitrogen restrains it at the end of the reaction, so that if both



retardations take place in a given oxidation, the curve expressing the resultant velocity might easily reduce to a straight line passing through the origin.

### *Conclusions.*

(1) A small quantity of water is necessary for the oxidation of phosphorus, and the reaction proceeds most rapidly when that quantity is present which is left after drying with sulphuric acid. When much water vapour is present, the action is considerably retarded.

(2) The formation of ozone and hydrogen peroxide requires the presence of excess of water; these substances are not direct products of the reaction between phosphorus and oxygen.

(3) Moderately dried phosphorus and oxygen react under all the pressures tried, and the phenomena of "false equilibrium" are not seen. The reaction may be divided into two stages: in the first, oxidation is slow and accompanied by a very feeble glow, the action being apparently unimolecular. The oxide formed is now under investigation. The second stage begins when the pressure falls below about 500 mm.: oxidation is continually accelerated until all the oxygen is absorbed, but no simple expression could be found connecting the velocity of the reaction with the pressure of oxygen. The glow is very bright and phosphorus pentoxide is formed. No satisfactory explanation of the phenomena of the second stage can yet be offered.

(4) When an inert gas, such as nitrogen, is present, the phenomena are substantially the same, but the acceleration of the second period ceases after a time and a retardation sets in. This is explained on a purely mechanical hypothesis.

(5) When phosphorus oxidises in moist oxygen, the reaction differs from that taking place in dry oxygen in the following respects:

(a) The oxidation does not begin until the oxygen pressure is less than about 500 mm.; when it does take place, it is slower, and is much retarded during the earlier part of the reaction. The retardation is explained as being due to a protective film formed in some, probably physical, manner by the water on the phosphorus.

(b) Ozone and hydrogen peroxide are produced, and ammonium nitrite and nitrate also, in the presence of nitrogen. None of the theories at present held completely accounts for these observations.

If the vapour pressure of water is 4—5 instead of 16—20 mm., the velocity curve does not greatly differ from that obtained in absence of water. And the difference observed in presence of the larger

quantity of water can readily be explained by assuming the formation of the protective film. There is no necessity to suppose that the primary reaction between the phosphorus and oxygen differs in the two cases.

The cost of some of the apparatus used in this investigation was defrayed by a grant from the Research Fund of the Society.

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WYE.

### CXXI.—*Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Sulphate. IV.*

By ROBERT SELBY MORRELL and JAMES MURRAY CROFTS.

IN former communications (Trans., 1899, 75, 786; 1900, 77, 1220; 1902, 81, 666), it has been shown that the action of hydrogen peroxide, in the presence of ferrous sulphate, on glucose, *d*-fructose, mannose, arabinose, rhamnose, and several other sugars results in the formation of osones, which were identified by the formation of osazones by the action of phenylhydrazine at the ordinary temperature; in the case of arabinose, the osone can be detected by the formation of phenylmethyalarabinosazone with phenylmethylhydrazine. We have investigated the action of *p*-bromophenylhydrazine on aqueous solutions of arabinosone and rhamnosone, at the ordinary temperature, and find that the corresponding osazones are formed, whilst arabinose and rhamnose react with the same base under similar conditions to give hydrazones. Phenylbenzylhydrazine has not yielded an osazone or a hydrazone with rhamnosone, but probably gives rise to a ketohydrazide. The explanation of this reaction must be that on concentrating an aqueous solution of an osone in the presence of traces of iron, oxidation of the osone to a keto-acid takes place. Besides the osones, various acids were formed in the oxidation of carbohydrates by hydrogen peroxide in the presence of ferrous sulphate, and these were removed by means of normal and basic lead acetates; the nature of these acids has now been investigated. In treating a sugar solution in order to obtain the osone, the quantity of hydrogen peroxide usually added corresponded with one gram-atom of available oxygen per gram-molecule of sugar; this was added in 1/10ths, and the temperature was kept as low as possible. If, however, more

peroxide (3 or 4 gram-mola.) is added and no precautions taken to ensure a slow action, the amount of acid products is increased.

So far as the action has been studied, the acids obtained from glucose and fructose are identical; this, on the whole, is to be expected, since each gives rise to glucosone. The acidic products identified are glycollic, glyoxylic, oxalic, and trihydroxybutyric acids; the occurrence of the first named, as a product from glucose, is peculiar and not readily explicable on the assumption that the sugar molecule is transformed into an osone before the carbon chain is broken. We intend to deal with this and other points of theoretical interest in a future communication.

#### EXPERIMENTAL.

##### *Action of Hydrogen Peroxide on Arabinose and Rhamnose in the presence of Ferrous Sulphate.*

In a former paper, it was also shown that arabinosone reacted with phenylmethylhydrazine to give the corresponding osazone (Trans., 1899, 75, 790). In a paper by Neuberg (*Zeit. Ver. Rubenzucker. Ind.*, 1902, 237), phenylmethylarabinosazone is described as having been obtained by the action of hydrogen peroxide on *d*-arabitol in the presence of ferrous sulphate and subsequent treatment with phenylmethylhydrazine. Neuberg states that it cannot be obtained from *d*-arabinose. The melting point given by us is 168—170°, which agrees with his numbers, 169—172°, and the analyses are quite satisfactory. Probably, Neuberg had an osone present, which then reacted readily with phenylmethylhydrazine to give phenylmethylarabinosazone.

It seemed to us advisable to try the action of other substituted hydrazines on the osones derived from arabinose and rhamnose, and we selected *p*-bromophenylhydrazine and phenylbenzylhydrazine.

##### *p*-Bromophenylarabinosazone.

An aqueous solution of arabinose containing 10 per cent. of the sugar, to which had been added 0.04 per cent. by weight of crystallised ferrous sulphate, was oxidised by hydrogen peroxide. The quantity of the peroxide used corresponded with 4 gram-atoms of oxygen for each gram-molecule of the sugar. The oxidising agent was introduced slowly and in small quantities at the ordinary temperature, care being taken that the ferric iron had passed back again to the ferrous state before more of the peroxide was added.

At the end of the oxidation, the nearly colourless solution was



treated with normal lead acetate, filtered from a small precipitate, and a saturated solution of tribasic lead acetate added in excess; a fairly large yellowish-white precipitate separated, which was collected. The precipitated lead salt furnished a calcium salt, which showed the following reactions of glyoxylic acid: a white precipitate with normal lead acetate or lime water, a red precipitate with phenylhydrazine acetate, and a yellowish-brown precipitate with a solution of aniline oxalate, after filtering from calcium oxalate. The calcium salt reduced Fehling's solution strongly at the ordinary temperature.

The filtrate from the lead salt was treated with more basic lead acetate and a sufficient quantity of baryta solution to precipitate the osone, together with any unattacked arabinose, in the form of the lead hydroxide compound.

The washed lead hydroxide compound was decomposed exactly by 50 per cent. sulphuric acid, and the filtrate gave no precipitate with either normal or basic lead acetate.

In order to prepare from the solution of the osone the phenylosazone (or *p*-bromophenylosazone), an acetic acid solution of the corresponding hydrazine was added either to the cold or to the slightly warmed solution. The osazone separated out immediately without further heating, the total yield of the phenylosazone being 30 per cent. of the weight of the arabinose taken. The arabinosazone, formed by the action of the phenylhydrazine, was entirely due to the presence of osone, because no free arabinose could be detected by *p*-bromophenylhydrazine or phenylmethylhydrazine, either of which would give a hydrazone.

The *p*-bromophenylosazone was prepared by adding a filtered acetic acid solution of *p*-bromophenylhydrazine to the aqueous solution of the osone, the base being kept in solution as much as possible by an excess of the acid. A red oil separated out immediately, which soon became solid and granular, the weight of the dark red precipitate amounting to 15 per cent. of the weight of the arabinose taken; the filtrate, when warmed on the water-bath for half an hour, gave a further amount of the osazone, the yield being 22 per cent. The osazone was very soluble in alcohol, ether, acetone, and ethyl acetate, but was sparingly soluble in chloroform and dissolved very slightly in hot benzene. After repeated crystallisation from benzene, it separated in spherular aggregates and melted at 171° with decomposition.

0.1447 gave 0.1119 AgBr. Br = 32.9.

0.1190 „ 11.5 c.c. moist nitrogen at 21° and 763 mm. N = 11.1.

0.1952 „ 0.3035 CO<sub>2</sub> and 0.0642 H<sub>2</sub>O. C = 42.4; H = 3.65.

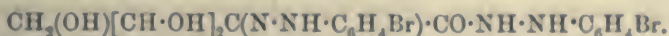
C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>N<sub>4</sub>Br<sub>2</sub> requires C = 41.97; H = 3.7; N = 11.5; Br = 32.9 per cent.

There seemed to be another substance present in the benzene solution which was more soluble in that solvent, and separated out from the mother liquors as a yellowish-brown, granular substance; it melted at  $112^{\circ}$  with decomposition and contained less nitrogen than the osazone.

0.1845 gave 17 c.c. moist nitrogen at  $20^{\circ}$  and 757 mm.  $N = 10.5$ .

$C_{17}H_{20}O_5N_4Br_2$  requires 10.7 per cent.

This substance is perhaps the hydrazide of the hydrazo-acid derived from arabinose,



The osazone did not possess the melting point and properties ascribed to *p*-bromophenyl-*L*-arabinoxazone by Neuberg (*Ber.*, 1899, 32, 3387).

In order to establish the identity of the foregoing osazone with that obtained from arabinose, it was prepared in the usual way, but, instead of recrystallising it from dilute alcohol, chloroform and benzene were used as solvents. The osazone separated from the benzene solution in a gelatinous form. After being dried in a vacuum, it was found to consist of spherular aggregates, which melted with decomposition at  $175^{\circ}$ , a considerably lower melting point than that given by Neuberg. There could be no doubt as to its purity, since 0.75 gram of the osazone required 200 c.c. of hot benzene for solution, and on cooling the osazone separated out almost immediately. Neuberg, who crystallised his osazone from alcohol, pointed out that, under different conditions, it existed in two forms.

In oxidising a sugar, it has been found that if the amount of hydrogen peroxide is increased, the melting point and percentage of nitrogen of the reaction product with hydrazines are diminished. This is most probably due either to the formation of a hydrazide or a hydrazo-acid, since the next oxidation product of an osone would be a keto-acid,  $CO_2H \cdot CO[CH \cdot OH]_2CH_2 \cdot OH$ .

#### *p*-Bromophenylrhamnosazone.

A 10 per cent. aqueous solution of rhamnose was oxidised by hydrogen peroxide in the presence of 0.04 per cent. of ferrous sulphate. The amount of hydrogen peroxide used was 4 gram-molecules for 1 gram-molecule of rhamnose. As in the case of the oxidation of arabinose, the peroxide was added very slowly with long intervals to allow the ferrous iron, which had been oxidised, to revert to the ferrous state. On treatment with normal lead acetate solution and filtration from a very small precipitate, addition of basic lead acetate caused only a slight turbidity. The osone was then precipitated from solution by



the addition of more basic lead acetate and baryta water. The washed precipitate was decomposed exactly by 50 per cent. sulphuric acid and the filtrate tested with phenylhydrazine acetate. The yield of osazone, which separated out partly at the ordinary temperature and partly on warming on the water-bath, amounted to 34 per cent. of the weight of the rhamnose. Here the osazone had been formed from the osone only, because the solution gave no *p*-bromophenylhydrazone at the ordinary temperature when tested with *p*-bromophenylhydrazine.

The *p*-bromophenylosazone was prepared in the same manner as the *p*-bromophenylarabinosazone, the yield calculated on the rhamnose being 20 per cent. After adding more of the base and prolonging the warming for half an hour on the water-bath, a further yield of 15 per cent. of the osazone was obtained. The substance was easily crystallised from dilute alcohol or from benzene, in which it was less soluble, and separated out in yellow aggregates of needles. It melted with decomposition at 215°, and analysis showed it to be an osazone.

0.2015 gave 0.3328 CO<sub>2</sub> and 0.0745 H<sub>2</sub>O. C = 43.69; H = 4.1.

0.1783 „ 17.3 c.c. moist nitrogen at 22° and 760 mm. N = 11.04.

0.1835 „ 0.140 AgBr. Br = 32.45.

C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>N<sub>4</sub>Br<sub>2</sub> requires C = 43.2; Br = 32; H = 4; N = 11.2 per cent.

#### *Rhamnose-p-bromophenylhydrazone.*

This substance was prepared by the action of *p*-bromophenylhydrazine acetate on an aqueous solution of rhamnose at the ordinary temperature. On recrystallisation from alcohol, the hydrazone was obtained in the form of rhomboidal plates which melted at 167° with decomposition.

On analysis, the substance was found to be the *p*-bromophenylhydrazone of rhamnose.

0.1952 gave 14.6 c.c. moist nitrogen at 18° and 767 mm. N = 8.71.

C<sub>12</sub>H<sub>17</sub>O<sub>4</sub>N<sub>2</sub>Br requires N = 8.4 per cent.

The filtrate from the hydrazone, when heated for one hour on the water-bath, yielded, on cooling, a yellow precipitate of aggregated needles which, after recrystallisation from dilute alcohol, melted at 215° with decomposition, and was identical in melting point and crystalline form with the osazone prepared from rhamnosone.

#### *Action of Phenylbenzylhydrazine on Rhamnosone.*

Rhamnose was oxidised by hydrogen peroxide in the presence of ferrous sulphate, according to the direction given above, but 1.5 gram-molecules of peroxide were used for 1 gram-molecule of the sugar.



The solution of the osone, when evaporated down to a small bulk under diminished pressure on the water-bath, was heated with an alcoholic solution of phenylbenzylhydrazine, and then concentrated to a syrup which was finally digested with cold benzene. This extract, when poured into light petroleum, yielded a yellow, amorphous substance which was exceedingly soluble in benzene and alcohol. Attempts to obtain it in a crystalline form from these solvents failed, and the substance, after being repeatedly dissolved in benzene and reprecipitated by petroleum ether, was analysed.

0.1693 gave 11.2 c.c. moist nitrogen at 15° and 757 mm.  $N = 7.74$ .

0.1497 „ 10 c.c. „ „ 17° and 755 mm.  $N = 7.74$ .

$\text{CH}_2[\text{CH}\cdot\text{OH}]_3\text{CO}\cdot\text{CONH}\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$  requires  $N = 7.87$ .

The melting point was very low, being between 50° and 60°, and the substance began to soften at the former temperature. The analytical results pointed more to the presence of a ketohydrazide than to that of a ketohydrazone. The existence of a hydrazone of an acid is unlikely, because, according to Lobry de Bruyn, phenylbenzylhydrazine does not react with ketoses. The phenylbenzylhydrazone of rhamnose can be obtained very easily in a crystalline form from either benzene, in which it dissolves sparingly, or from chloroform, in which it is more soluble. On concentrating a solution of an osone on the water-bath in the presence of traces of iron, the osones often become oxidised to an acid which reacts with phenylhydrazine to give substances which contain less nitrogen and also less carbon than the corresponding osazones. Most probably the rhamnosone has been oxidised further to  $\text{CH}_2[\text{CH}\cdot\text{OH}]_2\text{CO}\cdot\text{CO}_2\text{H}$ , which reacts with phenylbenzylhydrazine to give a ketohydrazide,  $\text{CH}_2[\text{CH}\cdot\text{OH}]_2\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ . Further evidence as to the existence of such a keto-acid must be left for another communication.

#### *The Precipitation of Rhamnose and Glucose from Aqueous Solutions by means of Lead Hydroxide.*

It was considered advisable to determine the amount of rhamnose and glucose precipitated from aqueous solution by basic lead acetate and baryta solution. In two estimations, twenty-five c.c. of a 1 per cent. solution gave 0.4135 and 0.4160 gram of copper from a Fehling's solution.

Nine grams of rhamnose were dissolved in 90 c.c. of water and the solution was treated with basic lead acetate and baryta solution; the precipitate was washed with cold water until the washings were free from barium and from lead, and then decomposed exactly by 50 per cent. sulphuric acid. The filtrate was made up to 200 c.c., and 25 c.c.

were withdrawn and boiled with excess of a Fehling's solution. In two estimations, the weights of reduced copper were, (1) 0.8583, (2) 0.8590. Therefore 4.154 grams of rhamnose had been precipitated with the lead hydroxide. In the case of glucose, under the same conditions, it was found that 38.5 per cent. of the glucose taken was precipitated with the lead hydroxide.

*The Acid Products of the Action of Hydrogen Peroxide on Glucose and d-Fructose in the presence of Ferrous Sulphate.*

Sixty grams of either glucose or *d*-fructose were dissolved in about 300 c.c. of distilled water and  $1\frac{1}{2}$  grams of crystallised ferrous sulphate were added; the hydrogen peroxide was added in quantities corresponding with 0.2 gram-atom of oxygen, until 4 gram-atoms of oxygen had been introduced. The solution had a strongly acid reaction and was partially neutralised by means of a solution of caustic soda. A saturated solution of normal lead acetate was then added, until no more precipitate was produced. After a short time, the whole was filtered; the precipitate contained oxalic, glyoxylic, and trihydroxybutyric acids in the form of their lead salts. After adding basic lead acetate solution to the filtrate, lead glycollate separated, the precipitate contained also varying, but small, quantities of the other acids, providing that this operation had been carefully performed. The well-washed precipitate of lead oxalate, glyoxylate, and trihydroxybutyrate was then decomposed exactly with dilute sulphuric acid, and the solution containing the free acids decolorised with animal charcoal and boiled with calcium carbonate. The calcium oxalate, which separated out immediately, was collected, purified by dissolving in hydrochloric acid and reprecipitating by ammonium hydroxide, and identified by an estimation of calcium.

The filtrate, which was still acid to litmus, was boiled with calcium carbonate until neutral, an operation which required some time owing to the presence of the lactone of trihydroxybutyric acid; the solution, as is always the case with the calcium salt of this acid, became very dark. Calcium glyoxylate was slowly deposited, which, however, was very dark in colour on account of the solution from which it was precipitated; it was purified by decomposition with oxalic acid, neutralisation with calcium carbonate, and evaporation of the solution to the crystallising point. When thus obtained, the salt had a greyish-white colour, and was slightly soluble in water; the solution gave, on warming, the characteristic red precipitate with phenylhydrazine acetate, and also a precipitate with lime water.

It was noticed that if the glyoxylic acid was only partially neutralised, the calcium salt was only partly deposited on evaporation;



more, however, came down when water, or preferably lime water, was added to the syrupy solution.

0.1090, dried at  $105^{\circ}$ , gave 0.085  $\text{CO}_2$  and 0.0316  $\text{H}_2\text{O}$ .  $\text{C} = 21.3$ ;  $\text{H} = 3.1$ .

0.1322 „  $110^{\circ}$ , gave 0.0804  $\text{CaSO}_4$ .  $\text{Ca} = 17.8$ .

$(\text{C}_2\text{H}_3\text{O}_4)_2\text{Ca}$  requires  $\text{Ca} = 18.0$ ;  $\text{C} = 21.6$ ;  $\text{H} = 2.7$  per cent.

The solution, after the separation of the calcium glyoxylate, contained practically only calcium trihydroxybutyrate. The calcium was removed exactly by oxalic acid, and from the acid filtrate the lead salt was precipitated by normal lead acetate solution. The analyses showed that the lead salt was nearly pure and gave numbers agreeing with those required for basic lead trihydroxybutyrate.

0.2617 lead salt lost 0.0227 on being dried at  $130^{\circ}$ .  $\text{H}_2\text{O} = 8.6$ .

$\text{C}_4\text{H}_6\text{O}_5\text{Pb}, 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.4$  per cent.

0.2390, dried at  $130^{\circ}$ , gave 0.2134  $\text{PbSO}_4$ .  $\text{Pb} = 60.5$ .

0.263, „  $130^{\circ}$ , „ 0.138  $\text{CO}_2$  and 0.0315  $\text{H}_2\text{O}$ .  $\text{C} = 14.3$ ;  
 $\text{H} = 1.33$ .

$\text{C}_4\text{H}_6\text{O}_5\text{Pb}$  requires  $\text{Pb} = 60.7$ .  $\text{C} = 14$ ;  $\text{H} = 1.7$  per cent.

The lead trihydroxybutyrate was transformed into the calcium salt, which gave on analysis the following numbers :

0.1509, dried at  $110^{\circ}$ , gave 0.068  $\text{CaSO}_4$ .  $\text{Ca} = 13.3$ .

$(\text{C}_4\text{H}_6\text{O}_5)_2\text{Ca}$  requires  $\text{Ca} = 12.98$  per cent.

The crude lead glycollate obtained, as described above, from the oxidised sugar solution, was decomposed with sulphuric acid, boiled with calcium carbonate, and allowed to deposit calcium glyoxylate. Any trihydroxybutyrate left was removed by the addition of a solution of normal lead acetate, and then basic lead glycollate was precipitated by basic lead acetate.

0.2023, dried at  $130^{\circ}$ , gave 0.2060  $\text{PbSO}_4$ .  $\text{Pb} = 69.5$ .

0.2000, „  $130^{\circ}$ , „ 0.063  $\text{CO}_2$  and 0.0198  $\text{H}_2\text{O}$ .  $\text{C} = 8.5$ ;  
 $\text{H} = 1.1$ .

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot \text{OH}$  requires  $\text{Pb} = 69.3$ .  $\text{C} = 8.1$ ;  $\text{H} = 1.3$  per cent.

The acid can be obtained from this salt by decomposing it with hydrogen sulphide; it gave a precipitate with normal lead acetate, but much less in quantity than with basic lead acetate, and the precipitate in each case was soluble in excess of the reagent and reprecipitated on adding water.

The acid darkened but did not reduce ammoniacal silver nitrate, was soluble in alcohol and ether, and could be obtained from the latter in a crystalline form. The calcium salt was easily obtained in



needle-shaped crystals by neutralising a hot solution of the acid with calcium carbonate.

Our thanks are due to the Research Fund Committee of the Chemical Society for a Grant to defray the expenses incurred in this investigation.

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CAMBRIDGE.

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## CXXII.—*Ethyl Benzylideneanilineacetoacetate.*

By ROBERT SELBY MORRELL and ALBERT ERNEST BELLARS.

It was formerly stated (Morrell and Crofts, Proc., 1898, 14, 121) that the purple oil, obtained by the action of anhydrous ferric chloride on ethyl acetoacetate, was decomposed by water into ferric chloride and ethyl acetoacetate, and that the ethyl acetoacetate yielded with benzylideneaniline an additive product melting at 78°. Schiff (*Ber.*, 1898, 31, 207) considered that the additive product melting at 78° was formed by the combination of the ketonic modification of ethyl acetoacetate with benzylideneaniline. The result obtained by Morrell and Crofts seemed to be anomalous, since the benzylideneaniline compound melting at 104° was expected, this temperature being the melting point of the compound obtained from the enolic form of ethyl acetoacetate and benzylideneaniline (Schiff, *loc. cit.*). Recently the existence of three forms of ethyl benzylideneanilineacetoacetate has been challenged by Rabe (*Ber.*, 1902, 35, 3947), who points out that aniline combines with ethyl benzylideneanilineacetoacetate to give a substance which melts at 78°. Rabe, who considered that the change of one form of ethyl benzylideneanilineacetoacetate into another form, as described by Schiff, was attended by the decomposition of the additive product with the liberation of aniline, had grave doubts as to the existence of three desmotropic modifications of ethyl benzylideneanilineacetoacetate.

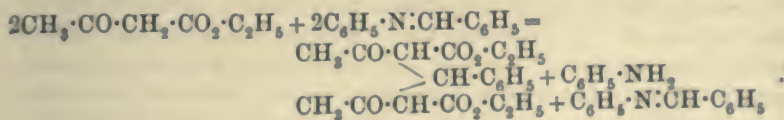
A few months ago, Francis (*Ber.*, 1903, 36, 937) published his investigations on the forms of ethyl benzylideneanilineacetoacetate, and concluded that one modification exists with a melting point of 104°, and perhaps a second modification melting at 78–80°.

With the intention of confirming the observation made on the ethyl benzylideneanilineacetoacetate obtained from the decomposition of the ferric chloride additive product, we tried a blank experiment with the specimen of ethyl acetoacetate used in our earlier work. The

ethyl acetoacetate was shaken with water and ether and then yielded, with benzylideneaniline, the modification melting at 78—80°. From this experiment, we were led to conclude that in this case the identification of an enolic or ketonic form by means of benzylideneaniline was not possible.

The formation of the ethyl benzylideneanilineacetoacetate under conditions which ought to have furnished a less fusible modification led us to repeat the work of Schiff, Rabe, and Francis on the influence of piperidine and of sodium ethoxide on the additive product of ethyl acetoacetate and benzylideneaniline.

As regards the influence of piperidine, the results agreed with those of Schiff and Francis, but not with those of Rabe. Sodium ethoxide had a singular effect; in the presence of a trace of the powdered reagent, the modification of ethyl benzylideneanilineacetoacetate melting at 78–80° was obtained. When the amount of sodium ethoxide was increased, a substance was produced which contained no nitrogen, and possessed the crystalline forms and melting points characteristic of a mixture of the  $\beta_1$  and  $\beta_2$  modifications of ethyl benzylidenediaceoacetate (Rabe, *Annalen*, 1900, 313, 176). The minimum amount of sodium ethoxide required to cause this change was found to be 0.03 gram for 1 gram of ethyl acetoacetate. It seemed that in the presence of a small quantity of sodium ethoxide the reaction could be represented by the following equation:



The aniline liberated in the reaction was detected by the same test which Rabe used (*Ber.*, 1902, 35, 3951). He showed that an alcoholic solution of freshly prepared ethyl benzylideneanilineacetate did not contain free aniline.

In our experiments, the ethyl benzylideneanilineacetoacetate melting at  $78-80^{\circ}$  has been obtained from freshly distilled ethyl acetoacetate, from samples of the esters which have been left for several years, and also from Kahlbaum's preparation, which is considered by Schiff to be the enolic form.

The results of our investigation point to the existence of one form of ethyl benzylidenedianilineacetate and show that the addition of small quantities of sodium ethoxide causes the formation of ethyl benzylidenediacetate. Ethyl benzylidenedianilineacetate (m. p. 78—80°) is quite stable and can be kept for a month without undergoing any change in its melting point.

It is essential that the benzene used for the recrystallisation of this



substance should be pure, inasmuch as a considerable elevation of the melting point is brought about by the use of the impure solvent (see p. 1295).

The peculiar action of small quantities of sodium ethoxide may perhaps account for the apparent existence of the less fusible modifications, since ethyl benzylidenediaceoacetate is soluble in the same solvents as ethyl benzylideneanilineaceoacetate.

The determination of the molecular weight of ethyl benzylideneanilineaceoacetate in benzene by Landsberger's method gave numbers agreeing with those obtained by Rabe and Biltz (R. Schiff, *Ber.*, 1898, 31, 208; 1902, 35, 4326; P. Rabe, *ibid.*, 1902, 35, 3951; W. Biltz, *ibid.*, 1902, 35, 4438; Francis, *ibid.*, 1903, 36, 941). The numbers suggested a gradual dissociation of the substance, since the molecular weight diminished with the dilution. In the case of carbon tetrachloride as solvent, the molecular weight of the ethyl benzylideneanilineaceoacetate diminished steadily with the dilution.

#### EXPERIMENTAL.

##### *Action of Benzylideneaniline on Ethyl Acetoacetate.*

A sample of redistilled ethyl acetoacetate, which had been used in the earlier work and had been kept for three years, was treated with one molecular proportion of benzylideneaniline (m. p. 48°). After some hours, the mixture, which had become quite solid, was powdered and washed with light petroleum; the yellowish-white solid was then found to melt at 84—85°, but after recrystallisation from benzene the melting point fell to 80°, and, when subsequently crystallised from carbon tetrachloride, it melted constantly at 78°.

In order to test a result obtained by one of us (*Proc.*, *loc. cit.*) in which the modification, melting at 78°, was obtained from the decomposition by water of the purple liquid produced by the action of anhydrous ferric chloride on ethyl acetoacetate and the subsequent treatment of the regenerated ethyl acetoacetate with benzylideneaniline, 1.7 grams of redistilled ethyl acetoacetate were dissolved in pure dry ether, the ethereal solution shaken with water, and the ethereal layer evaporated under reduced pressure at 30°. The ethyl acetoacetate was then dried in a vacuum and treated with benzylideneaniline under the foregoing conditions. The yellowish-white solid, when washed with light petroleum, was found to melt at 78°, and when crystallised successively from benzene and carbon tetrachloride the melting point remained constant at 80°. This experiment showed that the benzylideneaniline compound of ethyl acetoacetate, obtained from the ester regenerated from the ferric chloride compound, was the same



as that prepared by the action of benzylideneaniline on redistilled ethyl acetoacetate.

No conclusion as to the constitution of the ferric chloride compound with ethyl acetoacetate could be drawn from the study of the benzylideneaniline compound of the regenerated ethyl acetoacetate. As will be seen from the following results, freshly distilled ethyl acetoacetate with benzylideneaniline gave the more fusible modification. Freshly distilled ethyl acetoacetate (3.4 grams) was mixed with 5 grams of benzylideneaniline. The yellowish-white product, the yield of which was nearly quantitative, melted at  $75^{\circ}$  after washing with light petroleum; when crystallised from benzene, it melted at  $79^{\circ}$ , and on recrystallisation from carbon tetrachloride the melting point became constant between  $80^{\circ}$  and  $81^{\circ}$ .

0.3005 gave 12 c.c. moist nitrogen at  $23^{\circ}$  and 771 mm.  $N = 4.56$ .

$C_{19}H_{21}O_3N$  requires  $N = 4.5$  per cent.

When ethyl acetoacetate and benzylideneaniline were mixed in the proportion of two gram-molecules of the ethereal salt to one of the amine, the additive product obtained melted at  $78-80^{\circ}$  after successive crystallisations from benzene and carbon tetrachloride.

0.3762 gave 14.7 c.c. moist nitrogen at  $20^{\circ}$  and 771 mm.  $N = 4.54$ .

$C_{19}H_{21}O_3N$  requires  $N = 4.5$  per cent.

The specimen of ethyl acetoacetate supplied by Kahlbaum, and considered by Schiff to be the pure enolic form, yielded, on treatment with benzylideneaniline, an additive product, which, when washed with light petroleum, melted at  $83^{\circ}$ , and after successive crystallisations from benzene and carbon tetrachloride gave a constant melting point at  $81^{\circ}$ .

0.2512 gave 0.6735  $CO_2$  and 0.1525  $H_2O$ .  $C = 73.12$ ;  $H = 6.74$ .

$C_{19}H_{21}O_3N$  requires  $C = 73.33$ ;  $H = 6.7$  per cent.

The effect of impurities in the benzene on the melting point of the benzylideneaniline additive compound when crystallised from this solvent is illustrated by the following data:

The modification, m. p.  $78^{\circ}$ , after recrystallisation from redistilled but impure benzene, melted at  $98-99^{\circ}$ , and after recrystallisation from pure crystallisable benzene at  $87^{\circ}$ . In a duplicate experiment, the melting point after crystallisation from redistilled but impure benzene rose to  $86^{\circ}$ , whereas the substance melted at  $83^{\circ}$  when crystallised from pure crystallisable benzene.

The modification, m. p.  $81^{\circ}$ , when recrystallised from redistilled but impure benzene, melted at  $92-93^{\circ}$ , but the crystals separating from pure crystallisable benzene melted at  $85^{\circ}$ .

With ethereal or alcoholic ferric chloride, the additive product immediately gave a purple coloration, which was more intense in ether than in alcohol.

The influence of piperidine on the combination of benzylideneaniline and ethyl acetoacetate is stated by Schiff to bring about the formation of the modification melting at  $78^{\circ}$ . According to our results, piperidine did not influence the combination in the slightest degree. A mixture of 1.7 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 2 drops of piperidine became solid after a few hours, and the yellowish-white product, after being washed with ligroin, melted between  $72^{\circ}$  and  $73^{\circ}$ ; when crystallised from benzene, the substance melted at  $79^{\circ}$ , and the melting point remained at  $81$ – $82^{\circ}$  after crystallisation from carbon tetrachloride. The ligroin washings were found to contain free aniline. The numbers are practically the same as those obtained without the use of piperidine.

The influence of sodium ethoxide on the combination of benzylideneaniline and ethyl acetoacetate was very peculiar.\* According to Schiff, the addition of a very small quantity of sodium ethoxide causes the formation of the modification melting at  $104^{\circ}$ . Rabe states that sodium ethoxide decomposes the additive product, aniline being set free. We are able to confirm Rabe's statement, and, moreover, we find that in the presence of a trace of sodium ethoxide, and even in the absence of alcohol, aniline is eliminated from ethyl benzylideneanilineacetoacetate, giving rise to the formation of ethyl benzylidenediacetoacetate. A trace of sodium ethoxide did not influence the melting point of the modification, which was still between  $78^{\circ}$  and  $80^{\circ}$ , even when 0.06 gram of sodium ethoxide was employed with 6.4 grams of ethyl acetoacetate. If, however, 0.05 gram of sodium ethoxide was used with 1.7 grams of ethyl acetoacetate, the change in the melting point of the product was very marked.

(a) A mixture of 2.3 grams of ethyl acetoacetate, 3.3 grams of benzylideneaniline, and a trace of powdered sodium ethoxide became solid after some time, and the yellowish-white product, when washed with ligroin, was found to melt at  $92^{\circ}$ . After successive crystallisations from benzene and carbon tetrachloride, the melting point became constant between  $78^{\circ}$  and  $80^{\circ}$ .

(b) A mixture of 6.4 grams of ethyl acetoacetate, 7.5 grams of benzylideneaniline, and 0.06 gram of sodium ethoxide yielded, after several hours, a yellowish-white product which, when washed with ligroin, melted at  $77^{\circ}$ . After crystallisation from benzene, the melting point rose to  $79^{\circ}$ . Aniline was found in the ligroin and benzene washings,

\* The sodium ethoxide was prepared by the method described by Brühl and Biltz (*Ber.*, 1891, 24, 649), and dried in a vacuum at  $100^{\circ}$ .

and the mother liquor from the crystallisation in benzene gave, on adding ligroin, a substance which melted at  $89^{\circ}$ .

The ethyl benzylideneanilineacetoacetate, melting at  $79^{\circ}$ , was analysed with the following result:

0.1850 gave 0.4965  $\text{CO}_2$  and 0.1142  $\text{H}_2\text{O}$ .  $\text{C} = 73.19$ ;  $\text{H} = 6.85$ .

$\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$  requires  $\text{C} = 73.33$ ;  $\text{H} = 6.7$  per cent.

(c) The product obtained in a similar manner from 1.7 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 0.05 gram of sodium ethoxide, was, when washed with ligroin and crystallised from benzene, found to melt at  $124^{\circ}$ . Aniline was detected in the ligroin washings.

When alcohol was used instead of benzene, the product melted at  $150^{\circ}$ . The mother liquor from the benzene crystallisation gave, on the addition of ligroin, a substance which melted at  $140^{\circ}$ , whereas the compound obtained from the alcoholic mother liquor, on treatment with water, melted at  $128^{\circ}$ . The substance which melted at  $150^{\circ}$  was ethyl benzylidenedi-acetoacetate:

0.1560 gave 0.3750  $\text{CO}_2$  and 0.1015  $\text{H}_2\text{O}$ .  $\text{C} = 65.5$ ;  $\text{H} = 7.2$ .

$\text{C}_{19}\text{H}_{24}\text{O}_6$  requires  $\text{C} = 65.5$ ;  $\text{H} = 6.9$  per cent.

This compound, which is one of the forms of ethyl benzylidenedi-acetoacetate described by Rabe (*Annalen*, 1900, 313, 129), did not react with ferric chloride, and the aniline set free in its formation could be easily detected.

(d) The use of a larger amount of sodium ethoxide led to the formation of ethyl benzylidenedi-acetoacetate, as in the previous experiment, but the liquid mixture of benzylideneaniline and ethyl acetoacetate did not solidify and remained as a gelatinous mass. On treatment with ligroin, the gelatinous mass became solid, and after crystallisation from benzene or carbon tetrachloride the modification melted at  $123$ — $125^{\circ}$ , but after recrystallisation from alcohol the melting point rose to  $149$ — $150^{\circ}$ . The ethyl benzylidenedi-acetoacetate produced in this way was analysed with the following result:

0.25 gave 0.5912  $\text{CO}_2$  and 0.1549  $\text{H}_2\text{O}$ .  $\text{C} = 65.15$ ;  $\text{H} = 6.84$ .

$\text{C}_{19}\text{H}_{24}\text{O}_6$  requires  $\text{C} = 65.5$ ;  $\text{H} = 6.9$  per cent.

The alcoholic mother liquor from the crystals melting at  $149$ — $150^{\circ}$  gave, on dilution with water, a crystalline precipitate of flat, rhombic prisms which melted at  $137^{\circ}$ .

(e) A mixture of 2 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 0.1 gram of sodium ethoxide also yielded a gelatinous product which, after being washed with ligroin, melted at



136—138° and when recrystallised either from benzene or from carbon tetrachloride, melted at 134—136° or 131—133° respectively. The product contained no nitrogen, and an analysis showed that it was a mixture of the ketonic forms of ethyl benzylidenediacetoacetate.

0.2482 gave 0.5927 CO<sub>2</sub> and 0.1500 H<sub>2</sub>O. C = 65.1; H = 6.7.

C<sub>19</sub>H<sub>24</sub>O<sub>6</sub> requires C = 65.5; H = 6.9 per cent.

With a still larger quantity of sodium ethoxide, amounting to 0.5 gram for 2 grams of ethyl acetoacetate and 2.5 grams of benzylideneaniline, the gelatinous product, after being washed with ligroin, melted at 138—144°. On crystallisation from benzene, the melting point fell to 128—130°, and when recrystallised from carbon tetrachloride or alcohol the compound melted constantly at 130°. The substances with different melting point, but with the same chemical composition, were identical in crystalline form with those obtained by Rabe (*loc. cit.*). The modification melting at 130° was not homogeneous, but consisted of a mixture of acicular and rhomboidal crystals.

The variation in the values of the molecular weight of the benzylideneaniline additive product is of interest, as will be seen from the numbers obtained in the molecular weight determination by means of Landsberger's method.

|  |     |     |     |     |
|--|-----|-----|-----|-----|
| Molecular weight in benzene.....                               | 300 | 303 | 263 | 268 |
| Molecular weight in carbon tetrachloride...                    | 293 | 280 | 245 | 240 |
| C <sub>19</sub> H <sub>21</sub> O <sub>3</sub> N requires 311. |     |     |     |     |

These numbers suggest that a dissociation of ethyl benzylideneanilineacetate into its constituents occurs when it is heated to a temperature near its melting point in either benzene or carbon tetrachloride. From Rabe's work, we conclude that the constituents are aniline and ethyl benzylidenediacetoacetate. Biltz obtained the values 210 and 205 for the molecular weight in benzene by Landsberger's method. Rabe's values were 226 and 213, whilst those given by Francis are 292 and 305 in benzene and 302 and 232 in carbon tetrachloride.

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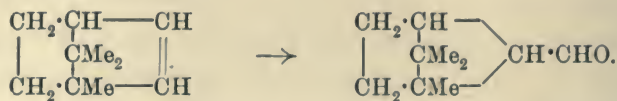
CXXIII.—*Contributions to the Chemistry of the Terpenes.*  
*Part I. The Oxidation of Pinene with Chromyl Chloride.*

By GEORGE GERALD HENDERSON and THOMAS GRAY.

IN the paper which contains an account of his investigation of the oxidising action of chromyl chloride on certain hydrocarbons (*Ann. Chim. Phys.*, 1881, [v], 22, 218), Étard states that some of the terpenes yield with that reagent solid addition products which are decomposed by water with the formation of camphoraldehydes. No details of his experiments are given in this paper, but in a later one (*Compt. rend.*, 1893, 116, 434) he describes more fully the results obtained by oxidising camphene and pinene with chromyl chloride. Each of these hydrocarbons was found to react with chromyl chloride, and the solid compounds which were formed yielded oily products when treated with water. The oil obtained from camphene combined with sodium hydrogen sulphite, and the crystalline bisulphite compound gave an aldehyde when decomposed in the usual manner. The aldehyde, to which Étard ascribed the formula  $C_{10}H_{14}O$ , resembled camphor in appearance, and was converted into a crystalline acid,  $C_{10}H_{14}O_2$ , when exposed to the air. From the oil obtained from pinene, Étard failed to prepare a crystalline compound with sodium hydrogen sulphite, and therefore purified it by distillation in a current of steam and subsequent fractionation in a vacuum. The product was an oily refractive liquid with an agreeable odour, which boiled at  $205-207^\circ$  (760 mm.) and showed the characteristic reactions of an aldehyde. Analysis gave  $C=79.5$ ,  $H=9.7$ ;  $C_{10}H_{14}O$  requires  $C=80.00$ ,  $H=9.33$ . The paper concludes with the following sentence: "Il n'est pas douteux qu'on puisse par le chlorure de chromyle transformer divers terpènes en aldéhydes et exceptionnellement en acétones."

Some years later, Bredt and Jagelki (*Annalen*, 1899, 310, 112) re-examined the action of chromyl chloride on camphene and showed that Étard's "camphenaldéhyde" and the acid which is formed from it by spontaneous oxidation are not unsaturated compounds, but in reality have the formulæ  $C_{10}H_{16}O$  and  $C_{10}H_{16}O_2$  respectively; for these substances they proposed the names camphenilanaldehyde and camphenilanic acid. They also found that camphenilanic acid is converted into an isomeride, *isocamphenilanic acid*, when boiled with dilute nitric acid, and that the latter is also obtained when the aldehyde is oxidised with dilute permanganate. They are of the opinion that camphene

is converted into camphenilanaldehyde in the manner indicated by the following formulæ:



Experiments on the action of chromyl chloride on pinene were also made by one of us (Trans., 1889, 55, 45), and it was proved that the solid additive compound has the formula  $\text{C}_{10}\text{H}_{16}, 2\text{CrO}_2\text{Cl}_2$ , and that the oily liquid obtained by the action of water on it does not consist of an aldehyde alone. However, the attempt to separate the mixture into its components was at that time unsuccessful.

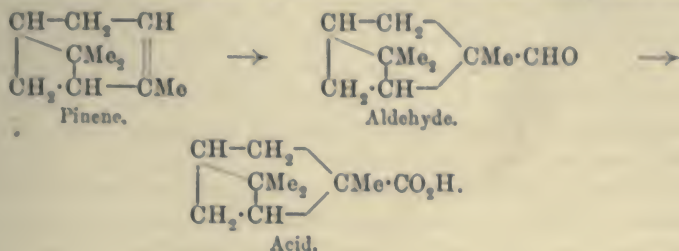
With the exception of the work summarised above, nothing has been done in this direction. We have recently returned to the subject, and intend to study the action of chromyl chloride on all the terpenes. The present paper contains an account of the results which we have hitherto obtained with pinene.

The solid compound, which is precipitated by adding a dilute solution of chromyl chloride in dry carbon disulphide to a similar solution of pinene, yields a viscid, brown oil when treated with water. When the oil is distilled in a current of steam, a large quantity of resinous matter remains in the distillation flask, and a clear, yellow, oily liquid volatilises with the steam. The yield is very small. This oily liquid is a mixture of at least three substances—a saturated *aldehyde*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , an unsaturated *ketone*,  $\text{C}_{10}\text{H}_{14}\text{O}$ , and a *chlorinated oxidation product* of pinene. The aldehyde is separated by means of its crystalline bisulphite compound, and the residual ketone is separated from the chlorinated compound, which has a considerably higher boiling point, by fractional distillation under diminished pressure. The ketone is present in largest quantity, whilst there is very little of the chlorinated compound. On exposure to air, the aldehyde is very quickly oxidised to the corresponding saturated *acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ . The same acid is obtained on oxidising the aldehyde with boiling dilute nitric acid or with dilute aqueous potassium permanganate, whence it is obvious that the aldehyde from pinene behaves differently in this respect from Bredt and Jagelki's camphenilanaldehyde. The quantity of the chlorinated product was too small to admit of purification, but an approximate analysis showed that it contains oxygen as well as chlorine.

A further study of the aldehyde and ketone, with which we are now occupied, is necessary before any conclusions with regard to their constitution are justifiable. However, if the action of chromyl chloride on pinene proceeds in a manner analogous to its action on camphene, and if Bredt and Jagelki's view of the constitution of camphenilanaldehyde



is correct, the formation of the pinene aldehyde and the corresponding acid should take place in the way indicated by the following formulæ :



### EXPERIMENTAL.

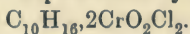
[With EWING SMITH, A.I.C.]

#### *Oxidation of Pinene with Chromyl Chloride.*

It was desirable that the chromyl chloride used in our experiments should be as far as possible free from chlorine, and therefore it was purified by two distillations under diminished pressure, the last in an atmosphere of dry carbon dioxide, and finally by passing a current of dry carbon dioxide through the gently heated liquid for a considerable time. In the first experiment, we used pure inactive pinene, prepared from a specimen of American oil of turpentine, for which we are indebted to the courtesy of Messrs. Barry, Ostlere, and Shepherd of Kirkcaldy. The turpentine was dried and distilled and the fraction boiling at 158—161° was converted into the nitrosochloride. The purified pinene nitrosochloride was decomposed by heating with aniline and alcohol, and the liberated pinene was extracted with ether, washed, dried, and distilled several times. The portion which boiled at 155—157° was used for the oxidation. Subsequent experiments showed that this tedious mode of purification was unnecessary, because the oil of turpentine, when repeatedly distilled, yielded a large fraction of pure *d*-pinene boiling at 156° (755 mm.), which, on oxidation, gave products quite as pure as those obtained from the pinene purified by means of the nitrosochloride. For the oxidation, ten per cent. solutions of chromyl chloride and pinene in dry carbon disulphide were employed. The solution of pinene (1 mol.) was placed in large flasks which were cooled by ice water, and the solution of chromyl chloride (rather more than 2 mols.) was added slowly in small quantities at a time, the mixture being well shaken after each addition. When the reaction was completed, the voluminous dark brown precipitate which had formed was washed by decantation with dry carbon disulphide until every trace of chromyl chloride had

been removed, drained quickly at the pump, and transferred to bottles. The pasty mass (a mixture of the precipitate with carbon disulphide) was then added in small portions to ice-cold water containing some sulphurous acid, and after each addition the flask was shaken until the solid was completely decomposed. In order to reduce the chromic acid which is formed by the action of water on the precipitate and thus to prevent any further oxidation of the product, some sulphur dioxide was passed into the solution from time to time. When the whole of the precipitate had been decomposed, the solution of the oxidation product in the carbon disulphide was separated from the upper aqueous layer, which was then extracted with more carbon disulphide. The carbon disulphide solution was thoroughly washed with water and the solvent was then removed by distillation, leaving the oxidation product in the form of a viscid, dark brown liquid having a pungent odour.

The solid compound, formed by the action of chromyl chloride on pinene, has the composition represented by the formula



When dry, it is a greyish-brown powder. It absorbs moisture with great avidity, and on exposure to the air is very quickly converted into a viscid, green liquid, which has a nauseous, sweet odour. It is completely decomposed by water, giving chromic chloride and chromic acid in addition to the organic substances.

#### *Separation of the Aldehyde, $\text{C}_9\text{H}_{15}\cdot\text{CHO}$ .*

The brown, oily substance obtained by decomposing the compound  $\text{C}_{10}\text{H}_{16}\cdot 2\text{CrO}_2\text{Cl}_2$  with water was distilled in a current of steam, when a large quantity of resin, which did not invite further examination, was left in the flask and a clear, yellow oil passed over into the receiver. The distillate was extracted with ether, the greater part of the ether removed by distillation, and the concentrated solution of the oil mixed with an equal volume of a saturated aqueous solution of sodium hydrogen sulphite. In our first experiment, a crystalline bisulphite compound was only formed very slowly after agitation of the mixture for about two days, but in subsequent preparations, crystallisation was easily started by the addition of a few particles of the compound. After separating the first crop of crystals, the ethereal liquid was shaken repeatedly with fresh quantities of the sulphite solution until no more crystals were formed. The *bisulphite compound* was collected at the pump (a troublesome process owing to the very finely crystalline condition of the substance) and washed thoroughly with alcohol and then with ether. It forms very minute, colourless crystals and is completely decomposed when heated with water. In order to obtain

the aldehyde, the bisulphite compound was boiled with aqueous sodium carbonate, the aldehyde, which volatilised with the steam and solidified in the receiver, was extracted with ether, the ethereal solution dried with calcium chloride, the ether distilled off, and the aldehyde finally purified by distillation in an atmosphere of carbon dioxide.

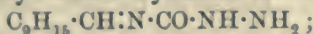
The *aldehyde*,  $C_9H_{15}\cdot CHO$ , is a soft, crystalline solid with a peculiar pungent odour. It melts at about  $33^\circ$  and boils at  $205-207^\circ$  (755 mm.) and volatilises very easily in a current of steam. It is practically insoluble in water, but very readily soluble in alcohol and in ether. It shows all the characteristic reactions of aldehydes, giving a coloration with magenta decolorised by sulphurous acid, reducing silver nitrate and uniting with sodium hydrogen sulphite. It oxidises spontaneously on exposure to the air, and with such rapidity that it is obtained in a state of purity only with some difficulty :

0.0964 gave 0.2790  $CO_2$  and 0.0922  $H_2O$ .  $C = 78.93$  ;  $H = 10.62$ .

0.1936 „ 0.5580  $CO_2$  „ 0.1825  $H_2O$ .  $C = 78.60$  ;  $H = 10.47$ .

$C_{10}H_{16}O$  requires  $C = 78.94$  ;  $H = 10.52$  per cent.

The aldehyde readily forms a crystalline *semicarbazone*,



this compound crystallises from methyl alcohol in lustrous, pearly leaflets and melts at  $191^\circ$  ; it is readily soluble in hot, but sparingly so in cold, methyl alcohol :

0.1582 gave 27.3 c.c. moist nitrogen at  $15^\circ$  and 764 mm.  $N = 20.33$ .

$C_{11}H_{19}ON_3$  requires  $N = 20.10$  per cent.

#### *Preparation of the Acid, $C_9H_{15}\cdot CO_2H$ .*

When the aldehyde is exposed to the air, it is very quickly oxidised to the *acid*,  $C_9H_{15}\cdot CO_2H$ , the same product being obtained when the oxidation of the aldehyde is effected either with boiling dilute nitric acid or with dilute aqueous potassium permanganate. After purification by conversion into the sodium salt, precipitation with dilute sulphuric acid, and crystallisation from dilute alcohol, the acid forms colourless, lustrous leaflets or flat prisms melting at  $117^\circ$  ; it is very sparingly soluble in water, but very easily so in alcohol or ether, and it volatilises slowly in a current of steam. The acid is a saturated compound, because it does not decolorise permanganate and does not combine additively with bromine. It is, however, attacked by bromine with the evolution of hydrogen bromide and formation of a substitution product :

0.2000 gave 0.5232  $CO_2$  and 0.1790  $H_2O$ .  $C = 71.34$  ;  $H = 9.94$ .

0.2000 „ 0.5230  $CO_2$  „ 0.1730  $H_2O$ .  $C = 71.31$  ;  $H = 9.61$ .

$C_{10}H_{16}O_2$  requires  $C = 71.42$  ;  $H = 9.52$  per cent.



The *lead* salt is precipitated as a white powder, soluble in boiling water. The *silver* salt,  $C_9H_{15}\cdot CO_2Ag$ , is also deposited as a white precipitate, very sparingly soluble in boiling water, from which it separates on cooling in small, colourless needles :

0.2840 gave 0.1114 silver.  $Ag = 39.22$ .

$C_{10}H_{15}O_2Ag$  requires  $Ag = 39.13$  per cent.

*Separation of the Ketone,  $C_9H_{14}\cdot CO$ .*

The ethereal solution of the oily oxidation product, from which the aldehyde had been removed by means of sodium hydrogen sulphite, was washed successively with aqueous sodium carbonate and water, and then dried with anhydrous calcium chloride. The solvent was then distilled off and the residual oil fractionally distilled under diminished pressure (90 mm.) in an atmosphere of dry carbon dioxide. After repeated distillations, it was finally separated into a large fraction boiling at  $131-133^\circ$  and a much smaller fraction boiling at  $145-150^\circ$ . The latter, which solidified on cooling, consisted mainly of the chlorinated compound. The large fraction, which consisted of the ketone, was warmed on a water-bath with moist silver oxide in order to remove the last traces of aldehyde, and then extracted with ether, washed, dried, freed from ether, and finally purified by distillation under atmospheric pressure.

The *ketone*,  $C_9H_{14}\cdot CO$ , is an almost colourless oily liquid with a pleasant aromatic odour. It is insoluble in water, but very readily soluble in the usual organic solvents. It boils at  $206-207^\circ$  (774 mm.). Its specific gravity at  $20^\circ$  is 0.9678, and its refractive index 1.477, and hence the molecular refraction is 43.8. The calculated molecular refraction for an unsaturated ketone having the formula  $C_{10}H_{14}O$  with one double linking is 43.7. The ketone at once decolorises permanganate and combines additively with 1 mol. of bromine. These results leave no doubt that it is an unsaturated compound containing one double linking :

0.1962 gave 0.5726  $CO_2$  and 0.1758  $H_2O$ .  $C = 79.59$  ;  $H = 9.96$ .

0.1410 „ 0.4124  $CO_2$  „ 0.1276  $H_2O$ .  $C = 79.77$  ;  $H = 10.05$ .\*

$C_{10}H_{14}O$  requires  $C = 80.00$  ;  $H = 9.33$  per cent.

With hydroxylamine, the ketone gives an oily *oxime*. The *semi-carbazone*,  $C_9H_{14}\cdot C:N\cdot CO\cdot NH\cdot NH_2$ , crystallises from methyl alcohol in minute, colourless needles, which begin to soften at about  $210^\circ$  and melt with decomposition at  $226-228^\circ$ . It is fairly easily soluble in hot, but sparingly so in cold methyl alcohol :

\* The difficulty of obtaining the ketone in a state of purity leaves these results open to revision.

0.1804 gave 31.7 c.c. moist nitrogen at 15° and 760 mm.  $N = 20.52$ .

$C_{11}H_{17}ON_3$  requires  $N = 20.29$  per cent.

The chlorinated oxidation product of pinene, which was separated from the ketone by fractional distillation under diminished pressure, was not obtained in sufficient quantity to admit of purification for analysis and examination. It is a crystalline solid which decomposes when heated under atmospheric pressure, but can be distilled under diminished pressure. It boils at about 145–150° (90 mm.) and is very readily soluble in alcohol or ether.

We are engaged in the fuller examination of the oxidation products of pinene described in the present paper, and also in studying the action of chromyl chloride on other terpenes. To begin with, we have selected limonene and sylvestrene as representatives of different groups of terpenes, and have found that these hydrocarbons also form solid additive products with chromyl chloride, which yield mixtures of aldehydes and ketones when decomposed with water.

We take this opportunity of expressing our thanks to Miss Ruth Pirret, B.Sc., for assistance in the earlier stage of this work, and to the Committee of the Carnegie Trust for a grant which defrayed the expenses.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

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#### CXXIV.—*Studies on Enzyme Action.* 1. *The Correlation of the Stereoisomeric $\alpha$ - and $\beta$ -Glucosides with the corresponding Glucoses.*

By E. FRANKLAND ARMSTRONG (Salters' Company's Research Fellow).

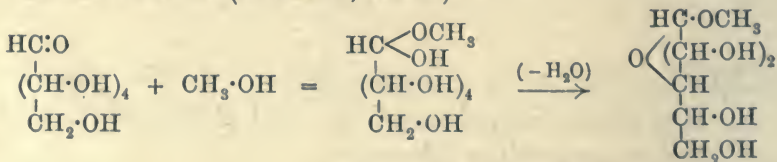
Of the explanations put forward of the change in rotatory power which glucose undergoes in solution—a phenomenon discovered by Dubrunfaut in 1846—the most probable is that suggested by Lowry (Trans., 1899, 75, 213), which connects the change of rotatory power of glucose with a reversible isomeric change. When this explanation was first given, it was not possible to decide definitely what formulæ were to be assigned to the dynamic isomerides. In view, however, of observations made during the investigation of various glucoside derivatives (Fischer and Armstrong, *Ber.*, 1901, 34, 2885; 1902, 35, 833, 3144 and 3153), in the course of which the existence of two undoubtedly stereoisomeric series of glucose derivatives was discovered

and their relationship to the  $\alpha$ - and  $\beta$ -methylglucosides established, it now seems probable that a lactonic structure may be assigned to the isomeric glucoses: these isomerides are, in fact, the two possible stereoisomeric lactones. From this point of view, the labile forms of glucose of high and low rotatory powers isolated by Tanret (*Compt. rend.*, 1895, 120, 1060), and called by him  $\alpha$ - and  $\gamma$ -glucose, are the parent substances of the  $\alpha$ - and  $\beta$ -glucosides whereas, as already pointed out by Lowry, his stable  $\beta$ -form of glucose is a mixture of the  $\alpha$ - and  $\gamma$ -isomerides in the proportion in which they are in equilibrium. Assuming this to be the case, the changes taking place in glucose—which occur slowly in simple aqueous solution but instantaneously in the presence of a small quantity of alkali—involve the passage from one or other form of the lactone into a mixture of both.

*Lactonic structure of glucosides.*—The following arguments may be adduced in support of the view that the  $\alpha$ - and  $\beta$ -glucosides are  $\gamma$ -lactones and that the isomerism is stereochemical.

(1) They do not combine with phenylhydrazine and therefore cannot contain an aldehyde group (E. Fischer, *Ber.*, 1893, 26, 2400).

(2) Even assuming that in the initial stage of the alkylation of glucose the latter is present in the aldehydic form, the separation of water at a subsequent stage necessarily involves the participation of a hydroxyl group attached to a carbon atom other than the terminal atom; in other words, it leads to the formation of a compound of lactonic structure (E. Fischer, *loc. cit.*).



(3) To judge from the non-formation of glucosidic derivatives from compounds such as benzoylcarbinol and benzoin—which contain the group  $\text{CO}\cdot\text{CH}\cdot\text{OH}$ —an  $\alpha$ -lactonic or ethylene oxide structure is practically excluded (E. Fischer, *loc. cit.*).

(4) On the other hand, the evidence accumulated by Fittig and others brings into prominence the tendency of hydroxy-acids to form  $\gamma$ -lactones wherever possible. Gluconic and similar acids have therefore been generally regarded as  $\gamma$ -lactones and the argument may fairly be extended to glucosides. The view put forward by Tollens (*Ber.*, 1883, 16, 921) that sugars in solution have a lactonic structure was based on this argument.

(5) W. H. Perkin, sen. (*Trans.*, 1902, 81, 177), in the course of his investigations on the magnetic rotatory power of the sugars, has



shown that glucose, galactose and the disaccharides maltose and lactose exhibit a rotatory power in agreement with that calculated on the assumption that they possess a lactonic structure.

(6) Inasmuch as the passage from glucose to the glucoside involves the production of a fifth asymmetric carbon atom, the existence of stereochemical isomerides may be anticipated.

(7)  $\alpha$ -Acetylchloroglucose and similar compounds are very easily converted into the  $\beta$ -modifications and *vice versa*: judging from the readiness with which this reversible change takes place, it is highly probable that the relationship is stereochemical (Fischer and Armstrong, *Ber.*, 1901, 34, 2885).

*Conversion of the Glucosides into the corresponding Glucoses.*

Assuming that Tanret's  $\alpha$ - and  $\gamma$ -glucoses represent the two possible stereoisomerides, it is only necessary, in order to determine their relationship to the  $\alpha$ - and  $\beta$ -glucosides, to convert the latter into the former by some method which does not involve the occurrence of isomeric change. Enzymes appeared to be the most likely agents to effect the desired changes without giving rise to secondary interactions; it is from this point of view that I have studied the action of emulsin, maltase, and invertase on a series of glucosides.

The  $\alpha$ - and  $\beta$ -alkylglucosides differ considerably in optical rotatory power, thus:

|                           | $[\alpha]_D$     |                          | $[\alpha]_D$  |
|---------------------------|------------------|--------------------------|---------------|
| $\alpha$ -methylglucoside | $= +157.5^\circ$ | $\beta$ -methylglucoside | $= -32^\circ$ |
| $\alpha$ -ethylglucoside  | $= +150.6^\circ$ | $\beta$ -ethylglucoside  | $= -30^\circ$ |

It is to be supposed that the same order of difference will be met with in the case of the glucoses. Obviously, Tanret's observations are in accord with this assumption and favour the view that  $\alpha$ - and  $\gamma$ -glucoses are to be correlated with the  $\alpha$ - and  $\beta$ -glucosides. Inasmuch as both forms are unstable in solution, the rotatory power of the glucose formed from a glucoside should change, falling considerably in the case of the  $\alpha$ -glucose and rising in that of the  $\beta$ -modification; as alkali brings about such a change at once, a sudden fall in the rotation on the addition of a trace of alkali would denote the presence of the  $\alpha$ -compound, whereas a sudden rise would indicate the  $\beta$ -compound.

The experiments made have in every case confirmed these views. Thus, in the case of the hydrolysis of  $\alpha$ -methylglucoside by means of maltase, the marked fall in the rotatory power, which was observed on adding ammonia, not only proves the formation of  $\alpha$ -glucose but also affords proof that the ordinary crystalline glucose of high rota-

tory power is  $\alpha$ -glucose, and should accordingly be correlated with the  $\alpha$ -glucosides.

In the case of experiments with  $\beta$ -methylglucoside and emulsin, a fall in rotatory power was observed on the addition of alkali; this observation shows that  $\beta$ -glucose is the immediate product of hydrolysis and makes it possible to correlate Tanret's solid  $\gamma$ -glucose with the  $\beta$ -glucosides.

The nature of the sugar first formed on hydrolysing some di- and tri-saccharides has been investigated in a similar manner.

When maltose—which has long been recognised as an  $\alpha$ -glucoside—is hydrolysed with maltase, a glucose is formed the rotatory power of which diminishes on the addition of ammonia; this again is a proof that the initial product of hydrolysis of  $\alpha$ -glucosides is  $\alpha$ -glucose.

When, in like manner, cane sugar—also an  $\alpha$ -glucoside—is hydrolysed with invertase, a mixture of glucose and lævulose is formed. The addition of ammonia to such solutions causes a marked diminution in the rotatory power, mainly due, no doubt, to the conversion of the  $\alpha$ -glucose initially formed into the mixture of constant rotatory power. Moreover, the change in the lævulose initially formed undoubtedly affects the rotatory power, but judging from the very small change in rotatory power which takes place in freshly prepared lævulose solutions, the magnitude of the change is relatively small. This observation confirms that previously made by O'Sullivan and Thompson (Trans., 1890, 57, 920).

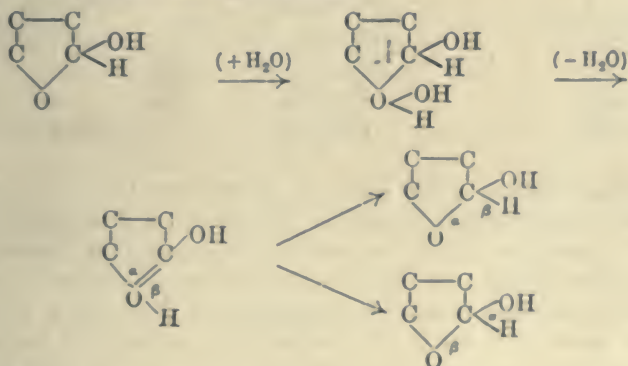
Lastly, when the trisaccharide, raffinose (derived from galactose, glucose and lævulose), is hydrolysed by invertase, a mixture of lævulose with the disaccharide melibiose is formed, which diminishes in rotatory power on the addition of ammonia. This result is evidence that melibiose is an  $\alpha$ -sugar; it may be mentioned that this is the first occasion on which the mutarotation of melibiose has been recorded.

In studying the action of diastase on cold starch paste, Brown and Morris (Trans., 1895, 67, 309) noticed that a rise in rotatory power took place on adding alkali, showing that the maltose produced was in the  $\beta$ -form. This conclusion involves the assumption that in the case of maltose, indeed of the sugars generally, the modification of low rotatory power is the  $\beta$ -form. The rotatory power of the only known maltoside,  $\beta$ -methylmaltoside ( $[\alpha]_D = +70^\circ$  approximately), is such as to support this supposition (Fischer and Armstrong, *Ber.*, 1901, 34, 2896; Königs and Knorr, *ibid.*, 3443). The ordinary solid form of maltose ( $[\alpha]_D +118^\circ$  initially, changing to  $[\alpha]_D +138^\circ$ ) must, from the same point of view, be regarded as the  $\beta$ -form; under normal conditions maltose separates from solution in this modification.

Other glucosides and polysaccharides are being tested in the same direction; the results obtained are already sufficient to show that glucosides and polysaccharides on hydrolysis form sugars of corresponding structure and that the sugars which exhibit the phenomenon of mutarotation have a lactonic structure.

*Nature of the Isomeric Changes,  $\alpha$ - $\rightleftharpoons$  $\beta$ -Glucoses.*

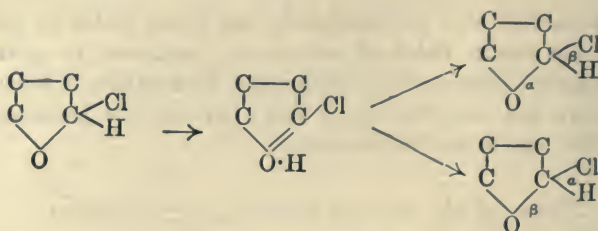
On the assumption that the glucoses are lactones, the isomerism may obviously arise in two ways: either it may be conditioned by the different relative position of the hydrogen atom and the hydroxyl group attached to the carbon atom which is in association with the lactonic oxygen, or it may arise from a difference in the position of the hydrogen atom relatively to the lactonic oxygen atom. The manner in which the change may be assumed to take place is represented by the following formulae:



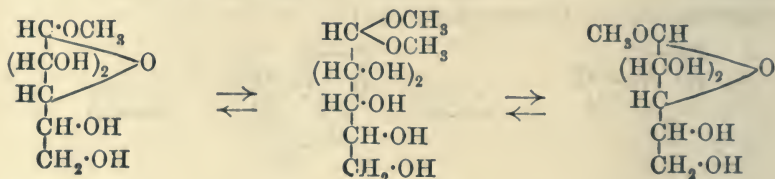
Apparently, the possibility of the latter form of isomerism has not hitherto been considered, although the behaviour of acetylchloroglucose is such as almost as to place the existence of this relationship beyond doubt.

When  $\alpha$ -acetylchloroglucose,  $[\alpha]_D + 193^\circ$ , dissolved in dry chloroform, is placed in contact with sodium hydroxide and a trace of water, it is to a large extent converted, in the course of a few weeks, into what must undoubtedly be regarded as the stereoisomeric  $\beta$ -compound,  $[\alpha]_D + 165^\circ$  (Fischer and Armstrong, *Ber.*, 1901 34, 2885). In this case, a change from the lactonic to the enolic type would involve the elimination and subsequent addition of hydrogen chloride, a migration which is inconceivable under such conditions. Isomerism must, therefore, be regarded as being conditioned by the interchange in position of the lactonic oxygen and hydrogen groups, somewhat in the following manner:





A similar explanation may be given of the partial conversion of  $\beta$ -pentacetylglucose into the  $\alpha$ -derivatives under the influence of zinc chloride (Erwig and Königs, *Ber.*, 1889, 22, 1464, 2207) and of  $\alpha$ - into  $\beta$ -methylglucosides and *vice versa* (*Ber.*, 1895, 28, 1146). In the latter case Fischer has assumed that an intermediate compound of the acetal type is produced and that the lactone ring is opened :



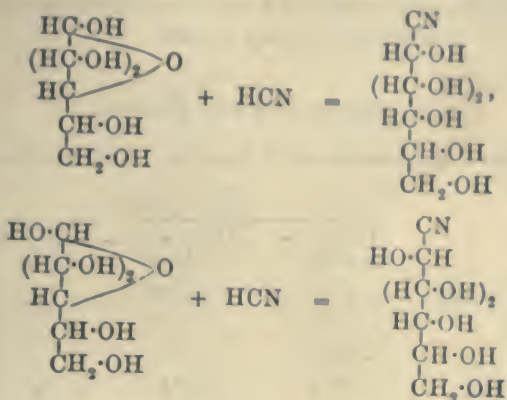
Jungius (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 99), who has recently determined the velocity with which the change takes place, however, considers it very improbable that an acetal is formed as an intermediate product ; he concludes that the two glucosides are directly converted into each other. This conclusion is in harmony with that deduced above in so far as it concerns the disruption of the lactone ring.

It should be pointed out in the case of glucose that, besides the above-mentioned changes occurring in the relative positions of the groups attached to the terminal carbon atom, another series of changes may take place involving enolisation and an interchange in the relative positions of the groups attached to the terminal and penultimate carbon atoms. The conversion of glucose into mannose and fructose probably involves changes of this order.

The view here established, namely, that glucose in solution is a mixture of two stereoisomeric lactones, affords a very simple explanation of several experimental facts observed in the sugar group.

Thus it is probable that the formation of two isomeric nitriles in unequal quantities when glucose, dissolved in water, combines with hydrogen cyanide merely involves the direct addition of hydrogen cyanide to the lactone ring of both modifications as shown below ; it is not necessary to assume that the hydrogen cyanide combines

selectively, as must be the case if it be supposed to combine with an aldehyde group:



As the action of enzymes on  $\alpha$ - and  $\beta$ -methylglucosides is selective, it is to be supposed that differences will be met with in the physiological behaviour of the  $\alpha$ - and  $\beta$ -modifications of sugars: thus it is conceivable that the one form of glucose would be fermented at least more easily than the other; it is proposed to test this view experimentally. Brown (British Association Report, Dover, 1899, p. 703) has already suggested that maltose in the form in which it is initially present when produced from starch may be fermented at a different rate than the optically stable form.

#### EXPERIMENTAL.

The solution of the enzyme having been prepared by extracting the dried enzyme with water and filtering several times, was mixed with a solution of the glucosides, and kept at a constant temperature. At stated intervals, about 7 c.c. were withdrawn by means of a pipette, rapidly filtered and examined in the polarimeter. In the case of invertase and similar rapidly acting enzymes, it was necessary to stop the hydrolysis before putting the solution in the polarimeter tube: this was effected by adding a drop of salicylaldehyde. After noting the angle of rotation, a drop of dilute ammonia was introduced into the solution and a new reading taken. Control experiments were made to ascertain the effect of minute quantities of salicylaldehyde or ammonia on the specific rotatory power of sugar solutions. Salicylaldehyde has no effect; ammonia, however, causes a slight diminution in the rotatory power of the reducing sugars, although it has no action on the glucosides.

Thus the rotatory power of a 10 per cent. glucose solution in a

1-dm. tube fell from  $+4.38^{\circ}$  to  $4.32^{\circ}$  on adding a drop of ammonia. In these experiments, however, as the quantity of reducing sugar present is always very small, the ammonia causes at the most a diminution of 2' or 3' in the rotatory power.

*$\beta$ -Methylglucoside and Emulsin.*

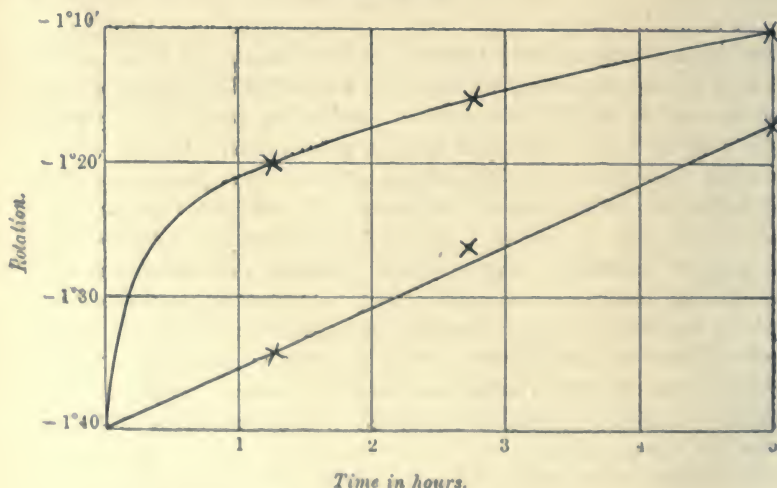
Concentration of glucoside = 5.4 per cent. Temperature =  $37^{\circ}$ .

| Time.      | Rotatory power. |                 |             |
|------------|-----------------|-----------------|-------------|
|            | Initial.        | Alkali added.   | Difference. |
| 0          | $-1^{\circ}40'$ | $-1^{\circ}40'$ | rise 0      |
| 1.25 hours | $-1^{\circ}34'$ | $-1^{\circ}20'$ | „ 14'       |
| 2.75 „     | $-1^{\circ}26'$ | $-1^{\circ}16'$ | „ 10'       |
| 5 „        | $-1^{\circ}17'$ | $-1^{\circ}10'$ | „ 7'        |
| 23 „       | $-0^{\circ}44'$ | $-0^{\circ}44'$ | „ 0'        |

Concentration of glucoside = 10 per cent. Temperature =  $37^{\circ}$ .

| Time.  | Rotatory power. |                 |             |
|--------|-----------------|-----------------|-------------|
|        | Initial.        | Alkali added.   | Difference. |
| 0 hour | $-2^{\circ}30'$ | $-2^{\circ}30'$ |             |
| 0.25 „ | $-2^{\circ}23'$ | $-2^{\circ}9'$  | rise 14'    |
| 0.5 „  | $-2^{\circ}18'$ | $-2^{\circ}6'$  | „ 12'       |
| 1.0 „  | $-2^{\circ}10'$ | $-2^{\circ}0'$  | „ 10'       |

The change in rotatory power on the addition of alkali is very clearly expressed in the following curve.





*$\alpha$ -Methylglucoside and Maltase.*

Concentration of glucoside = 10 per cent. Temperature = 27°.

| Time.   | Rotatory power. |               |             |
|---------|-----------------|---------------|-------------|
|         | Initial.        | Alkali added. | Difference. |
| 0 hour  | + 15°6'         | + 15°6'       |             |
| 0.5 "   | + 15°           | + 14°41'      | fall 19'    |
| 1 "     | + 14°50'        | + 14°16'      | " 34'       |
| 2 hours | + 14°36'        | + 13°40'      | " 56'       |

*Maltose and Maltase.*

Concentration of disaccharide = 10 per cent. Temperature = 27°.

| Time.   | Rotatory power. |               |             |
|---------|-----------------|---------------|-------------|
|         | Initial.        | Alkali added. | Difference. |
| 0 hour  | + 11°38'        | + 11°33'      | fall 5'     |
| 0.5 "   | + 11°14'        | + 10°52'      | " 22'       |
| 1 "     | + 11°0'         | + 10°24'      | " 36'       |
| 2 hours | + 10°33'        | + 10°1'       | " 32'       |

*Cane Sugar and Invertase.*

Concentration of disaccharide = 10 per cent. Temperature = 17°.

| Time.   | Rotatory power. |               |             |
|---------|-----------------|---------------|-------------|
|         | Initial.        | Alkali added. | Difference. |
| 0 hour  | + 5°12'         | + 5°12'       |             |
| 0.5 "   | + 4°32'         | + 3°59'       | fall 33'    |
| 1 "     | + 3°48'         | + 3°1'        | " 47'       |
| 2 hours | + 2°1'          | + 1°20'       | " 41'       |
| 3 "     | + 0°30'         | - 0°4'        | " 34'       |
| 4.75 "  | - 1°9'          | - 1°27'       | " 18'       |

*Raffinose and Invertase.*

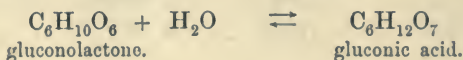
Concentration of trisaccharide = 5 per cent. Temperature = 17°.

| Time.     | Rotatory power. |               |             |
|-----------|-----------------|---------------|-------------|
|           | Initial.        | Alkali added. | Difference. |
| 0.5 hour  | + 5°23'         | + 4°47'       | fall 36'    |
| 1.0 "     | + 4°50'         | + 4°18'       | " 32'       |
| 2.5 hours | + 3°42'         | + 3°20'       | " 22'       |

CXXV.—*Studies of Dynamic Isomerism. I. The Mutarotation of Glucose.*

By T. MARTIN LOWRY, D.Sc.

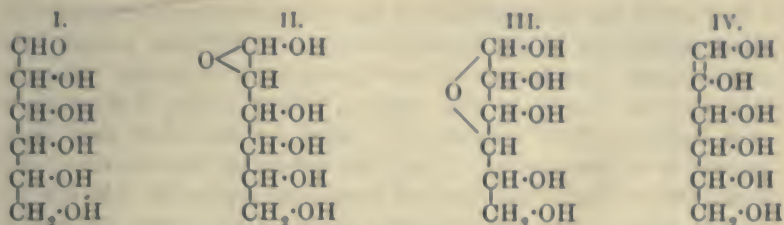
THE gradual change in the rotatory power of freshly prepared aqueous solutions of glucose, observed by Dubrunfant in 1846, was at first regarded as being due to purely physical causes. The chemical character of the phenomenon was not recognised until Emil Fischer, in 1890, discovered that similar changes of rotatory power were produced by the partial hydrolysis, in aqueous solution, of optically active lactones and suggested that the mutarotation of glucose might be due to the conversion of the sugar by combination with water into a heptahydric alcohol of lower rotatory power :



This theory explained all that was known of the mutarotatory sugars until Tanret, in 1896, showed that it was possible to isolate, not only ordinary  $\alpha$ -glucose,  $[\alpha]_D +105^\circ$ , and the  $\beta$ -glucose,  $[\alpha]_D +52.5^\circ$ , into which it passes in solution, but also a  $\gamma$ -glucose of low rotatory power,  $[\alpha]_D +22^\circ$ , which was also convertible into  $\beta$ -glucose;  $\gamma$ -glucose proved to be isomeric with  $\alpha$ -glucose, not the hydrate which Fischer's theory indicated.

Three years later, nitrocamphor was observed to undergo changes of rotatory power which were undoubtedly due to reversible isomeric change; it then became clear that mutarotation was a normal accompaniment of dynamic isomerism in optically active substances, although similar effects might be produced by reversible polymeric change or by association with the solvent. The application to the case of glucose was obvious: Tanret's  $\alpha$ - and  $\gamma$ -glucose were dynamic isomerides; his  $\beta$ -glucose was not a third isomeride, as he had supposed, but a mixture in equilibrium of the  $\alpha$ - and  $\gamma$ -forms.

At that time, it was not possible to assign definite formulæ to the isodynamic glucoses; in addition to the aldehydic formula, two oxide formulæ, II and III, had been proposed, each representing two stereoisomerides, and an enolic modification, IV, was not impossible; any two of these possible compounds might exhibit dynamic isomerism and give rise to mutarotation :



For purely chemical reasons, the ethylene oxide formula for glucose has been generally abandoned; the enolic form, as will be shown later, can scarcely be present except in minute quantities; it is therefore probable that the main constituents have an aldehydic or a  $\gamma$ -oxide structure: indeed this view has been held by Lippmann, Tanret and others. Quite recently, Simon (*Compt. rend.*, 1901, 132, 487—490) has suggested that  $\alpha$ - and  $\gamma$ -glucoses are the lower homologues of  $\alpha$ - and  $\beta$ -methylglucosides respectively, and supports this view by referring to the specific rotatory power of the four substances:

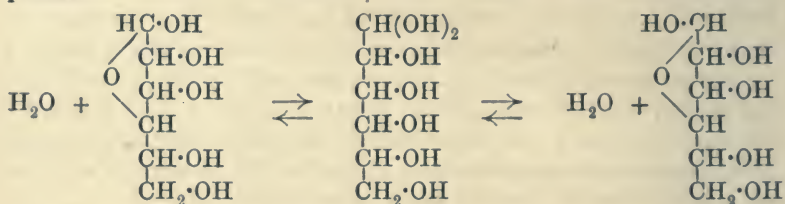
|                         |         |                |         |
|-------------------------|---------|----------------|---------|
| α-Methylglucoside ..... | + 157°  | α-Glucose..... | + 105°  |
| β-Methylglucoside.....  | - 32    | γ-Glucose..... | + 22    |
| Mean                    | + 62·5° |                | + 63·5° |

This theory accords with the fact that  $\alpha$ - and  $\gamma$ -glucoses can both be crystallised from solution, a property specially characteristic of sugar derivatives containing a  $\gamma$ -oxide ring, and is, moreover, much more probable than the alternative view that the aldehyde is in equilibrium with only one of the stereoisomeric  $\gamma$ -oxides. A direct proof of the glucosidic structure of  $\alpha$ - and  $\gamma$ -glucoses was, however, wanting; this is now afforded by the experiments which Dr. E. F. Armstrong describes in the preceding paper. The actual production from  $\beta$ -methylglucoside of a glucose of low initial rotatory power, whilst the  $\alpha$ -glucosides yield a sugar of high rotatory power, affords very strong evidence in favour of the  $\gamma$ -oxide formulæ which had been provisionally assigned to  $\alpha$ - and  $\gamma$ -glucoses.

Simon, like Lippmann (*Ber.*, 1896, 29, 203) and Tanret (*Bull. Soc. Chim.*, 1896, iii, 15, 195), regards  $\beta$ -glucose as a third isomeride, ascribing the mutarotation of  $\alpha$ - and  $\gamma$ -glucoses to their (complete) conversion into the isomeric aldehyde. Such a view is directly opposed to the theory of dynamic isomerism, which postulates a reversible isomeric change in which both isomerides are converted into a mixture in equilibrium of the two forms; it is, moreover, not in agreement with the experimental data, for if the change into the aldehyde were complete it would be impossible by mere crystallisation to reconvert this into the  $\alpha$ -glucose which normally separates from the solution.

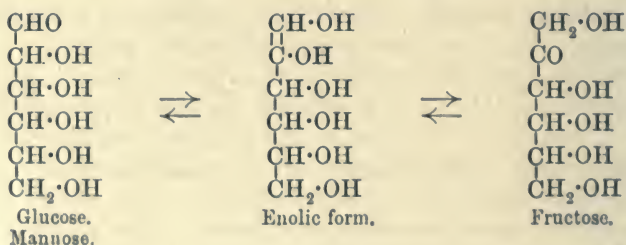


But whilst the mutarotation of the glucoses must be regarded as being mainly due to the establishment of equilibrium between the stereoisomeric  $\gamma$ -oxides, it is not improbable that the aldehyde may also be present in the mixture, either in the free state or as a hydrate. This conclusion is based on the view that it is impossible to interchange directly the points of attachment of the H and OH radicles; the simplest mechanism by which this can be brought about is that which involves the breaking of the  $\gamma$ -oxide ring and the formation of the aldehyde or its hydrate as an intermediate product :



If this view be correct the conversion of  $\alpha$ - into  $\gamma$ -glucose involves a two-fold change, and can only proceed rapidly if the aldehyde be formed with considerable velocity and be present in appreciable quantity in the solution.

A similar argument may be used to show that only traces of the enolic form are present. Glucose, fructose and mannose have a common enolic form :



and, as Lobry de Bruyn has shown (*Rec. trav. chim.*, 1895, 14, 201), are convertible into one another in alkaline solution. But whilst  $\alpha$ - and  $\gamma$ -glucose reach a condition of equilibrium in a few hours when merely dissolved in water or instantaneously in the presence of a mere trace of alkali, mannose, glucose and fructose are changed only slowly and incompletely in the presence of large amounts of the catalyst. This excessively slow conversion indicates clearly that the enolic form can be produced only at a very slow rate and in the most minute proportions.

The mutarotation of nitrocamphor in neutral solvents having been found to depend on the presence of traces of some third substance (*Trans.*, 1899, 75, 219), it was of interest to find whether the

mutarotation of aqueous solutions of glucose were not also conditioned by associated impurities. In view of the great sensitiveness of glucose to alkaline catalysts and the impossibility of preparing and keeping "pure" water in glass vessels, the preparation of a "pure" solution of glucose which should not exhibit mutarotation was not undertaken. But as neutral salts have little or no influence on the change, it was thought that the mutarotation might be checked or altogether prevented by neutralising any acid or basic impurities present in the solution.

Before attempting such a neutralisation, it was necessary to ascertain (1) the extent to which the activity of acids and bases could be destroyed by neutralisation; (2) the amount of acid or base required to account for the rate of change normally observed. On the former point, the evidence was conclusive: the rotatory power of a 5 per cent. solution of glucose in normal potassium chloride decreased somewhat less rapidly than that of a simple aqueous solution, the change at  $11^{\circ}$  being half completed in 1.9 hours in the former and in 1.8 hours in the latter case; a decinormal solution showed a greater retardation but this was perhaps due to some slight contamination of the aqueous solution used for comparison.

Quantitative experiments on the influence of acids, the results of which are plotted in Fig. 1 (p. 1318), showed that whilst the change in a 5 per cent. solution of glucose in  $N/10$  hydrochloric acid was half complete in 0.27 hour at  $14^{\circ}$ , the corresponding period for  $N/100$  hydrochloric acid was 0.7 hour, and for a simple aqueous solution, 0.9 hour at  $15^{\circ}$ . Osaka (*Zeit. physikal. Chem.*, 1900, 35, 661—706) has shown that the effects produced by acids are proportional to the square root of the concentration, so that doubling the amount of acid increases the velocity by about 40 per cent.; as the actual increase produced by  $N/100$  hydrochloric acid was only 30 per cent., if the mutarotation were dependent on acid impurities these must be present to a greater extent than  $N/100$  in the 5 per cent. solution. This is obviously not the case, inasmuch as not only is the solution not appreciably acid but it responds readily to the addition of quantities of alkali which would be completely neutralised by much smaller proportions of acid impurity.

Quantitative experiments on the influence of alkali brought out in a very striking way the extraordinary sensitiveness of glucose to these agents, a fact to which numerous experimenters have called attention. Whilst  $N/100$  hydrochloric acid produced only a slight acceleration, the equivalent quantity of caustic potash brought about so rapid a change that equilibrium had already been attained when the first reading of the polarimeter was taken only four minutes after preparing the solution. A solution in  $N/1000$  caustic potash showed an equally remarkable acceleration: the isomeric change at  $11^{\circ}$  was half com-

pleted at the end of five minutes, and equilibrium was reached in little more than half an hour. A distinct acceleration was produced even by  $N/10000$  caustic potash, the action being half completed in 0.8 hour, whilst a solution in  $N/100000$  caustic potash and a comparison solution in water each required 1.5 hours. Osaka has shown that the effects produced by alkalis are directly proportional to the concentration, a result which is confirmed by the values given above for  $N/1000$  and  $N/10000$  caustic potash. The velocity of

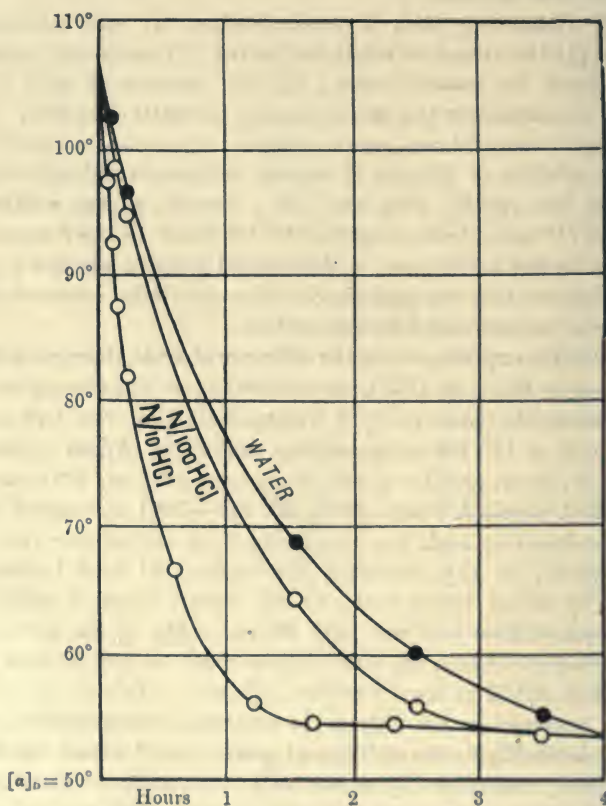


FIG. 1.—Influence of acids on the mutarotation of glucose.

isomeric change is doubled by the addition of  $N/10000$  caustic potash, so that if the mutarotation of the aqueous solution were due to an alkaline impurity this need only be present to the extent of  $N/10000$  in the 5 per cent. solution. Even this small amount of alkali could not be derived from the water, which had a specific conductivity of only 0.000002 reciprocal ohms per cubic centimetre at  $18^\circ$ , whilst  $N/10000$  caustic potash gave the value 0.000056. The glucose solution, how-



ever, in spite of an increase of some 10 per cent. in its viscosity as compared with water, had a conductivity 0.000052 at 18°. This is probably due in part to the feebly acid properties of the sugar but might have been caused by associated alkali. Attempts were therefore made to check the mutarotation by the addition of acids: in a comparative experiment, using 5 per cent. solutions of glucose in (1) water, (2) *N*/10000 hydrochloric acid and (3) *N*/1000 hydrochloric acid—

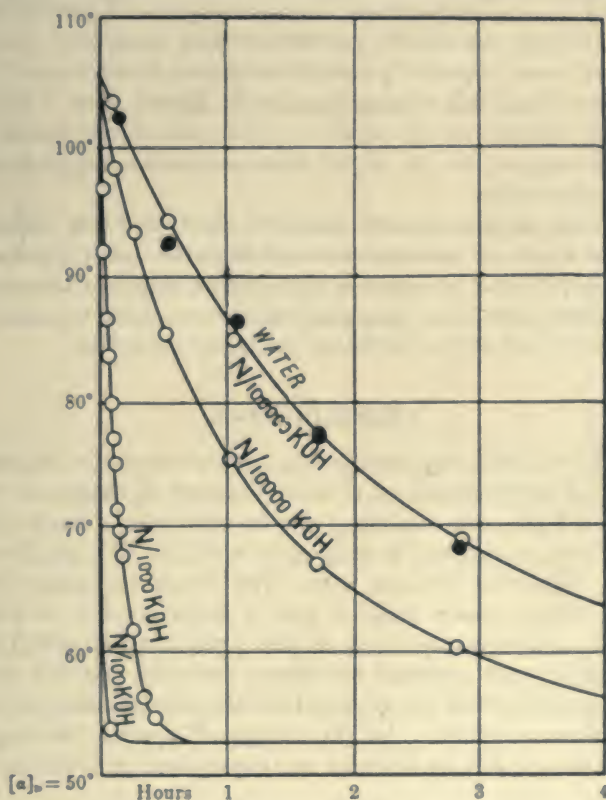


FIG. 2.—Influence of alkalis on the mutarotation of glucose.

the amounts of acid present were too small to produce any specific acceleration, but more than sufficient to neutralise all alkaline impurities—the numerical results were so closely in agreement that it was not possible to represent them by separate curves.\*

\* At the end of three hours, the solutions gave identical values (67.0, 67.0, and 66.8), but the readings at one hour and two hours indicated that the aqueous solution had changed a trifle more rapidly and was perhaps five minutes in advance of

It is therefore clear that the mutarotation of glucose cannot be checked by neutralisation and is not dependent on the presence of acid or basic impurities in the aqueous solution. This result was somewhat unexpected and indicates a behaviour quite different from that of nitrocamphor dissolved in chloroform. The difference may perhaps be ascribed to the fact that water is an ionising solvent. When solvents of this class were used, labile solutions of nitrocamphor were never obtained, and indeed such solutions could scarcely be expected to withstand the catalytic action of the strongly acid *pseudonitro*-compound. It may, however, be pointed out that, apart from its ionising properties, water is probably directly concerned in the isomeric change of glucose since this change appears to depend upon a process of reversible hydrolysis; chloroform, on the other hand, merely brings the nitrocamphor into the liquid state and cannot assist directly in the isomeric change.

Whilst the experiments now described show that the mutarotation of glucose is not due to alkaline or acid impurities, they give no indication of the probable behaviour of pure glucose dissolved in pure water: if the solution could by extreme purification be rendered non-conducting, it is possible that the mutarotation would not take place.

#### EXPERIMENTAL.

In order to obtain comparable results at atmospheric temperatures, the method adopted was to observe the rate of change of rotatory power of a 5 per cent. solution of glucose containing a known quantity of acid, base, or salt, and to compare it with that of a simple aqueous solution prepared at the same time. The change was usually complete in about 8 hours, and a series of half a dozen readings of each tube was taken at intervals of about an hour; the solutions which changed more rapidly were observed at shorter intervals, and the curve for  $N/1000$  caustic potash was plotted from observations made at intervals of less than a minute. As the change of specific rotatory power amounts to over  $50^\circ$ , no difficulty was experienced in obtaining smooth curves.

The *glucose* used was a commercial "pure" sample from Kahlbaum; the solutions prepared from it gave normal values for the specific rotatory power, and no alteration was produced by recrystallising twice from dilute methyl alcohol. As recrystallisation produced no retardation in the velocity of change, the commercial sample was used in all the remaining experiments.

The *water* had been purified (for conductivity measurements) by the acid solutions; this may be merely accidental, but might also indicate that a trace of alkaline dirt, amounting to about  $N/200000$ , had been neutralised and the velocity of isomeric change thus slightly reduced, in the acid solutions.

process of continuous fractional distillation, and had a conductivity of 0 000002 reciprocal ohms per cubic centimetre.

The *potassium chloride* was purified by crystallising until it gave solutions of constant conductivity; the normal solution prepared from the fused salt had a conductivity which agreed exactly with that given by Kohlrausch, Holborn, and Dusseldorf.

The *hydrochloric acid* was prepared by absorbing a weighed quantity of the dry gas in purified water.

The *caustic potash* was the purest commercial alkali containing no alumina or silica, and was freed from carbonate by means of purified baryta.

The values observed in 5 per cent. solutions of glucose were as follows :

## I.

| (a) Commercial glucose. |              | (b) Recrystallised glucose. |              |
|-------------------------|--------------|-----------------------------|--------------|
| Time.                   | $[\alpha]_D$ | Time.                       | $[\alpha]_D$ |
| 6 m.                    | 98.5°        | —                           | —            |
| 10 m.                   | 96.0         | 10 m.                       | 98.3°        |
| 55 m.                   | 76.7         | 49 m.                       | 80.3         |
| 1 h. 38 m.              | 67.2         | 1 h. 38 m.                  | 68.7         |
| 2 h. 18 m.              | 61.7         | 2 h. 18 m.                  | 62.7         |
| 4 h. 10 m.              | 54.7         | 4 h. 0 m.                   | 55.2         |

Temperature 17.5°.

Half-period..... (a) 0.82 h. (b) 0.71 h.

## II.

| (a) Water. |              | (b) N/10 KCl. |              | N/10 HCl.  |              |
|------------|--------------|---------------|--------------|------------|--------------|
| Time.      | $[\alpha]_D$ | Time.         | $[\alpha]_D$ | Time.      | $[\alpha]_D$ |
| 11 m.      | 94.8°        | 9 m.          | 100.8°       | 4 m.       | 97.3°        |
| 15 m.      | 92.5         | 14 m.         | 96.0         | 6 m.       | 92.3         |
| 26 m.      | 87.3         | 31 m.         | 87.8         | 8 m.       | 87.3         |
| 42 m.      | 81.3         | 47 m.         | 82.8         | 13 m.      | 81.8         |
| 1 h. 3 m.  | 75.7         | 1 h. 9 m.     | 77.7         | 34 m.      | 67.5         |
| 1 h. 40 m. | 67.7         | 1 h. 48 m.    | 70.7         | 48 m.      | 62.2         |
| 2 h. 22 m. | 63.0         | 2 h. 29 m.    | 66.3         | 1 h. 12 m. | 56.0         |
| 3 h. 48 m. | 57.7         | 3 h. 53 m.    | 59.7         | 1 h. 40 m. | 54.3         |
| 6 h. 24 m. | 53.0         | 6 h. 32 m.    | 53.7         | 2 h. 20 m. | 54.2         |
| next day.  | 52.0         | next day.     | 52.3         | next day.  | 53.3         |

Temperature 14°.

Half-period intervals..... (a) 0.82 h. (b) 1.0 h. (c) 0.27 h.



## III.

| (a) Water. |                | (b) Normal KCl. |                |
|------------|----------------|-----------------|----------------|
| Time.      | $[\alpha]_D$ . | Time.           | $[\alpha]_D$ . |
| 8 m.       | 104.7°         | 8 m.            | 105.5°         |
| 17 m.      | 100.0          | 20 m.           | 101.0          |
| 51 m.      | 90.8           | 52 m.           | 91.7           |
| 2 h. 22 m. | 74.3           | 2 h. 24 m.      | 75.5           |
| 3 h. 18 m. | 68.5           | 3 h. 21 m.      | 69.2           |
| 4 h. 15 m. | 63.8           | 4 h. 17 m.      | 64.7           |
| 4 h. 59 m. | 61.0           | 5 h. 7 m.       | 61.5           |
| 6 h. 39 m. | 57.2           | 6 h. 42 m.      | 57.2           |
| next day.  | 53.3           | next day.       | 52.7           |

Temperature 11°.

Half-period..... (a) 1.8 h. (b) 1.9 h.

## IV.

| (a) Water. |                | (b) N/100 HCl. |                |
|------------|----------------|----------------|----------------|
| Time.      | $[\alpha]_D$ . | Time.          | $[\alpha]_D$ . |
| 6 m.       | 102.3°         | 8 m.           | 98.5°          |
| 13 m.      | 96.6           | 13 m.          | 94.7           |
| 1 h. 33 m. | 68.6           | 1 h. 32 m.     | 64.0           |
| 2 h. 30 m. | 60.0           | 2 h. 30 m.     | 55.7           |
| 3 h. 30 m. | 55.0           | 3 h. 30 m.     | 53.3           |

Temperature 14°.

Half-period..... (a) 0.9 h. (b) 0.7 h.

There was some uncertainty as to the zero reading of the polarimeter during this series, but this would affect the values for both solutions to an equal extent.

## V.

| (a) Water. |              | (b) N/10000 HCl. |              | (c) N/1000 HCl. |              |
|------------|--------------|------------------|--------------|-----------------|--------------|
| Time.      | $[\alpha]_D$ | Time.            | $[\alpha]_D$ | Time.           | $[\alpha]_D$ |
| 10 m.      | 101.5°       | 10 m.            | 102.3°       | 10 m.           | 101.8°       |
| 58 m.      | 84.8         | 58 m.            | 85.5         | 58 m.           | 86.5         |
| 2 h. 4 m.  | 73.3         | 2 h. 2 m.        | 75.0         | 2 h. 3 m.       | 74.8         |
| 3 h. 5 m.  | 67.0         | 3 h. 5 m.        | 66.8         | 3 h. 5 m.       | 67.0         |
| 4 h. 24 m. | 61.5         | 4 h. 24 m.       | 61.2         | 4 h. 24 m.      | 60.8         |
| next day.  | 52.8         | next day.        | 53.3         | next day.       | 52.8         |

## VI.

| (a) Water. |              | (b) N/100000 KOH. |              | (c) N/10000 KOH. |              |
|------------|--------------|-------------------|--------------|------------------|--------------|
| Time.      | $[\alpha]_D$ | Time.             | $[\alpha]_D$ | Time.            | $[\alpha]_D$ |
| 9 m.       | 102.5°       | 6 m.              | 103.7°       | 6 m.             | 98.5°        |
| 33 m.      | 92.8         | 33 m.             | 94.5         | 16 m.            | 93.5         |
| 1 h. 4 m.  | 86.5         | 1 h. 3 m.         | 85.0         | 32 m.            | 86.3         |
| 1 h. 43 m. | 77.2         | 1 h. 43 m.        | 77.5         | 1 h. 2 m.        | 75.2         |
| 2 h. 51 m. | 68.2         | 2 h. 52 m.        | 69.0         | 1 h. 42 m.       | 67.0         |
| next day.  | 52.7         | next day.         | 54.2         | 2 h. 50 m.       | 60.2         |
|            |              |                   |              | next day.        | 52.7         |

| (d) N/1000 KOH. |              | N/1000 KOH. |              | (e) N/100 KOH. |              |
|-----------------|--------------|-------------|--------------|----------------|--------------|
| Time.           | $[\alpha]_D$ | Time.       | $[\alpha]_D$ | Time.          | $[\alpha]_D$ |
| 1.5 m.          | 97.0°        | 7 m.        | 74.0°        | 4 m.           | 53.5°        |
| 2 m.            | 92.0         | 8 m.        | 71.2         |                |              |
| 2.5 m.          | 89.8         | 9 m.        | 69.8         |                |              |
| 3 m.            | 86.7         | 10 m.       | 67.8         |                |              |
| 3.5 m.          | 86.2         | 15 m.       | 61.7         |                |              |
| 4 m.            | 83.8         | 20 m.       | 56.3         |                |              |
| 5 m.            | 80.0         | 26 m.       | 54.7         |                |              |
| 6 m.            | 77.0         | next day.   | 52.7         |                |              |

Temperature 11° C.

Half period ..... (a) and (b) 1.50 h. (c) 0.8 h. (d) 0.08 h.  
 (e) probably about 0.008 h = 30 secs.

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CXXVI.—*The Rotatory Power of Maldiamide, Maldin-propylamide, and Maldibenzylamide.*

By JOHN McCRAE.

THE researches of Frankland and his pupils and others have clearly demonstrated that by the introduction of the radicles of fatty acids and of aromatic acids into the esters of active hydroxy-acids the effect produced, so far as rotatory power is concerned, depends on the nature of the group introduced. In the case of diethyl tartrate, the introduction of two fatty acyl groups either slightly increases or only slightly diminishes the rotatory power (Freundler, *Ann. chim. phys.*, 1894, [vii], 3, 433; Frankland and Patterson, *Trans.*, 1898, 73, 181; Frankland and Turnbull, *ibid.*, 203; McCrae and Patterson, *Trans.*, 1900, 77, 1096; compare also McCrae, *Trans.*, 1901, 79, 1103), but if the acyl groups introduced are those of an aromatic acid, the dextro-rotation of the original ester is changed into a high lævo-rotation (Freundler, *loc. cit.*; Frankland and Wharton, *Trans.*, 1896, 69, 1309, 1583; Guye and Babel, *Arch. Sci. phys. nat. Genève*, 1899, [iv], 7, 23; compare also McCrae, *loc. cit.*).

It has been shown (McCrae and Patterson, *loc. cit.*; compare also Freundler, *loc. cit.*) that when two phenacetyl groups are introduced, the effect produced is similar to that brought about by the fatty acyl radicles, and not to that caused by the aromatic groups. Similar observations have been made in other series.

In the case cited, the alkyl radicles are attached to the active nucleus through a carbonyl group, and the following observations were made in order to find whether or not the same effect is produced when the alkyl groups are united with the active nucleus through an imino-group.

For the purpose in view, malic acid was selected, and its diamide, di-*n*-propylamide, and dibenzylamide were prepared and studied. The first has already been polarimetrically examined by Walden (*Zeit. physikal. Chem.*, 1895, 17, 264), but a re-examination was made in the same solvents as those used for the other compounds in order to obtain comparable values.

## EXPERIMENTAL.

The diethyl *L*-malate used in the preparation of the following compounds was obtained by the Fischer method described by Reitter (*Zeit. physikal. Chem.*, 1901, 36, 135); it had a rotation of  $-11.53^\circ$  ( $l=1$ ,  $t=15^\circ$ ).



*l-Maldiamide*.—This was prepared according to Pasteur's method (*Jahresber.*, 1851, 411) by saturating a solution of diethyl malate in absolute alcohol with dry ammonia in the cold. After three or four days, the maldiamide separated, and when crystallised from hot absolute alcohol it melted at 157°.

*l-Maldi-n-propylamide*.—Five grams of *n*-propylamine and 7.5 grams of diethyl malate were heated together in a sealed tube at 60° for an hour and a half. The product, which solidifies on cooling, was dried on a porous tile and then melted at 116–120°. It is easily soluble in water, alcohol, ether, or chloroform, and is best crystallised from hot benzene, as it is only sparingly soluble in this solvent when cold. The purified substance melts at 125.5°, the yield being 60 per cent.

0.1580 gave 18.0 c.c. of nitrogen at 20° and 758 mm.  $N = 13.29$ .

$C_{10}H_{20}O_3N_2$  requires  $N = 12.91$  per cent.

*l-Maldibenzylamide*.—By heating together 7 grams of benzylamine and 5 grams of diethylmalate in a sealed tube at 70–80° for several hours, 8.1 grams of crude maldibenzylamide melting at 151° were obtained, the yield being 97 per cent. The diamide can be recrystallised from water or chloroform, but it separated most readily from benzene; the crystals, which are prismatic, melt at 155.5°.

0.1772 gave 14.25 c.c. of nitrogen at 17.5° and 760 mm.  $N = 9.47$ .

$C_{18}H_{20}O_3N_2$  requires  $N = 8.98$  per cent.

In order to be able to compare the rotatory powers of these compounds with the corresponding dianilide and ditoluidides examined by Walden (*loc. cit.*) and by Guye and Babel (*loc. cit.*), the rotation was determined in glacial acetic acid and in pyridine solutions. The results obtained are tabulated on p. 1326, the rotations and the densities being both determined at the temperature given. In the author's experiments, the length of the polarimeter tube was 198.5 mm. The table also contains the numbers obtained by Walden and by Guye and Babel.

### Conclusions.

The profound influence of the solvent on the rotatory power is demonstrated by the foregoing data; as a rule, the rotation is higher in pyridine solution than in acetic acid, but maldi-*n*-propylamide is an exception, for it shows a somewhat higher rotation in the latter solution.

Comparing the specific rotations, it is seen that the replacement of a hydrogen atom of each of the amino-groups of maldiamide by

|                                      | Tem-<br>perature. | Grams of<br>substance<br>in 100 c.c.<br>of solution. | Density. | Ob-<br>served<br>rotation. | Specific<br>rotation. | Mole-<br>cular<br>rotation. |
|--------------------------------------|-------------------|--|----------|----------------------------|-----------------------|-----------------------------|
|                                      | t°.               | c.   | d.       | $\alpha_D$ .               | $[\alpha]_D$ .        | $[M]_D$ .                   |
| <i>Solvent: glacial acetic acid.</i> |                   |  |          |                            |                       |                             |
| Maldiamide .....                     | 20°               | 4.678  | 1.0652   | -4°12'                     | -45.2°                | -59.7°                      |
| Maldi- <i>n</i> -propylamide..       | 19                | 4.798  | 1.0525   | -4 28                      | -46.9                 | -101.3                      |
|                                      | 16                | 4.977  | 1.0552   | -4 41                      | -47.4                 | -102.4                      |
| Maldibenzylamide.....                | 22                | 4.654  | 1.0560   | -1 52                      | -20.2                 | -63.0                       |
| *Maldianilide .....                  | —                 | 1.50   | —        | —                          | -60.7                 | -172.4                      |
| *Maldi- <i>o</i> -toluidide.....     | —                 | 2.00   | —        | —                          | -65.0                 | -202.8                      |
| *Maldi- <i>p</i> -toluidide ...      | —                 | 1.00   | —        | —                          | -70.0                 | -218.4                      |
| <i>Solvent: pyridine.</i>            |                   |  |          |                            |                       |                             |
| Maldiamide .....                     | 17°               | 1.998  | 1.0002   | -2°18'                     | -57.7°                | -76.2°                      |
| Maldi- <i>n</i> -propylamide..       | 17                | 4.789  | 0.9973   | -3 59                      | -41.9                 | -90.5                       |
| Maldibenzylamide.....                | 15                | 4.855  | 1.0028   | -3 7                       | -32.4                 | -101.1                      |
| †Maldianilide .....                  | —                 | 4.825  | —        | —                          | -101.1                | -287.1                      |
| †Maldi- <i>o</i> -toluidide.....     | —                 | 4.82   | —        | —                          | -61.8                 | -192.8                      |
| †Maldi- <i>m</i> -toluidide ...      | —                 | 4.82   | —        | —                          | -75.9                 | -236.8                      |
| †Maldi- <i>p</i> -toluidide ...      | —                 | 4.82   | —        | —                          | -92.5                 | -288.6                      |

\* Determined by Walden.

† Determined by Guye and Babel.

*n*-propyl or benzyl either scarcely alters the rotatory power or actually diminishes it.

On comparing the tabulated results, it is seen that the introduction of aromatic groups into the amino-groups of maldiamide exerts a very different quantitative effect from that caused by the replacement of the hydrogen of the amino-groups by fatty radicles. The difference, although not so clearly marked as in the case of diethyl tartrate, is, nevertheless, quite distinct, and, as the replacement takes place in a different part of the molecule, it was hardly to be expected that the difference in the effects would be so great; with the amides in question, the replacement takes place at a point further removed from the active carbon atom than in the case of the tartrates cited, and, consequently, its effect on the rotation should not be so great (Guye and Babel, *Arch. Sci. phys. nat. Genève*, 1899, [iii], 7, 114, and Guye, *Trans.*, 1901, 79, 476).

The results also show that the benzyl group approximates in its effect much more closely to the fatty than to the aromatic radicles, and this establishes the fact that the different influences referred to

in connection with diethyl tartrate are in no way due to the presence of the carbonyl group beyond its negative character, which will, of course, persist in all the compounds. This conclusion is not at all surprising, since it is known, from physico-chemical measurements and also from the chemical deportment of the benzyl radicle, that this group is to be classed with the fatty rather than with the aromatic radicles.

I am indebted to the Committee of the Chemical Society Research Fund for assistance in procuring the materials used in this investigation, and I desire to express my thanks to Prof. Stroud of the Yorkshire College for kindly placing his polarimeter at my disposal.

QUEEN MARGARET'S COLLEGE,  
GLASGOW.

## CXXVII.—*The Constitution of Chrysophanic Acid and of Emodin.*

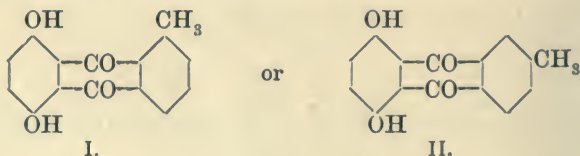
By HOOPER ALBERT DICKINSON JOWETT and CHARLES ETTY POTTER.

ALTHOUGH chrysophanic acid and emodin have long been known to be respectively the di- and tri-hydroxy-derivatives of a methylanthraquinone, the position of the substituting groups has remained undetermined. The exact constitution of these substances is, however, of considerable importance from a pharmacological standpoint, inasmuch as they occur naturally in several drugs possessing a cathartic action. Hesse (*Annalen*, 1899, 309, 32) has suggested certain formulæ for these substances, but he adduces no evidence, either theoretical or experimental, in support of his assumptions. The object of this investigation was to determine the position of the substituting groups, and, if possible, to synthesise the substances themselves. Although we have failed to accomplish these syntheses we are able, with a considerable degree of certainty, to propose formulæ for both these compounds.

Chrysophanic acid yields, on distillation with zinc dust, a product which Liebermann (*Annalen*, 1876, 183, 159) considered to be 2-methylanthracene, but owing to the great similarity which exists between the isomeric methylanthracenes this point cannot be considered as being definitely proved. Chrysophanic acid was not methylated, even when treated with excess of sodium and methyl iodide in methyl alcohol at 100° (Jowett and Potter, *Trans.*, 1902, 81, 1584). It

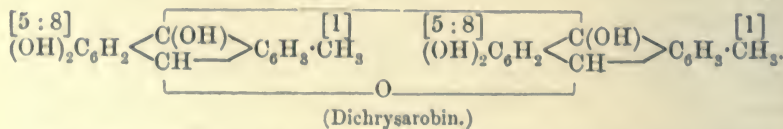
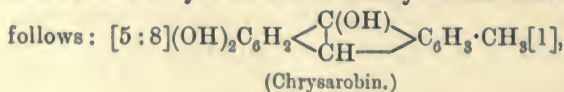


follows that both hydroxyls must be contiguous to a carbonyl group in the anthraquinone molecule. Furthermore, by fusion with caustic alkali or by oxidation with permanganate, it does not yield any derivative of benzoic acid, but gives rise only to simple oxidation products such as oxalic acid, from which it may be concluded that the hydroxyl groups are attached to one benzene residue and the methyl radicle to the other. If all three substituting groups were attached to one benzene residue or a hydroxyl to one and the methyl radicle and a hydroxyl to the other, fusion with caustic alkali would certainly furnish either benzoic acid or one of its derivatives (Liebermann, *Ber.*, 1879, 12, 1293). Moreover, the methyl radicle attached to one benzene residue and the quinol group present in the other afford to oxidising agents two points of attack, and furnish an explanation of the ease with which disruption of the molecule occurs. The only possible formulæ for chrysophanic acid are therefore



5:8-Dihydroxy-2-methylantraquinone (formula II) has, however, been synthesised (Niementowski, *Ber.*, 1900, 33, 1634), and appears to coincide in physical and chemical characters with chrysophanic acid. As it seemed likely that the possibility of the identity of the synthetical and natural products had been overlooked, we prepared some 5:8-dihydroxy-2-methylantraquinone and found that it was not identical with chrysophanic acid. Formula II must therefore be abandoned, and we may regard I as the constitutional formula of chrysophanic acid, which is that previously suggested by Hesse (*loc. cit.*).

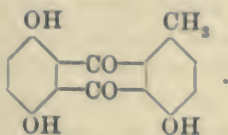
If this formula for chrysophanic acid is accepted, it necessarily follows that chrysarobin and dichrysarobin must be represented as follows:



We have endeavoured to synthesise 5:8-dihydroxy-1-methylantraquinone by the condensation of hydroxysalicylic acid with *o*- and with *m*-toluic acids and of 1-methylphthalic anhydride with quinol, but in

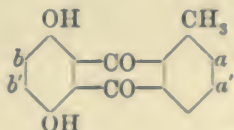
all cases without success. The failure in the latter case is inexplicable, as 2-methylphthalic anhydride readily condenses with quinol.

Hesse has also suggested the following formula for emodin :

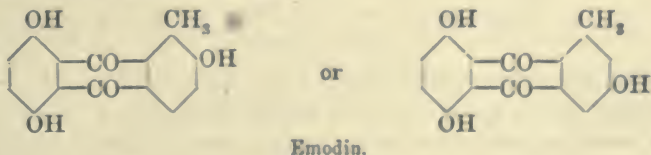


This, however, is incorrect, as emodin yields a monomethyl ether, which would not be the case if the three hydroxyl groups occupied the positions indicated in the above formula. It follows that one hydroxyl group in emodin occupies the meta-position with regard to a carbonyl residue. There are three reasons why emodin should be regarded as a hydroxyl derivative of chrysophanic acid : (1) as both substances occur together in certain plants, notably rhubarb, it is most probable that both contain the same complex, and differ only by the presence of an additional hydroxyl group in emodin ; (2) both chrysophanic acid and emodin behave similarly when fused with caustic alkali or when oxidised with permanganate, neither yielding any derivative of benzoic acid ; (3) emodin, on distillation with zinc dust, yields a methyl-anthracene, which is regarded by Liebermann as being the 2-methyl compound, whereas Perkin (*Trans.*, 1894, 65, 925) supposes it to be the 1-methyl derivative.

If it is admitted that emodin contains the chrysophanic acid residue, then the additional hydroxyl must occupy one of the following positions *a*, *a'*, *b*, or *b'* :

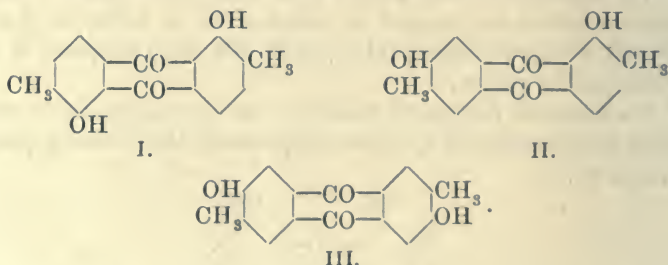


If the third hydroxyl in emodin occupied position *b* or *b'*, we should expect to find indications of dyeing properties, owing to the position of the two contiguous hydroxyl groups with respect to the carbonyl radicle. Emodin, however, has been shown to be quite devoid of these properties. It is therefore most probable that the additional hydroxyl group occupies position *a* or *a'*, and emodin would thus be represented by one of the following formulæ :



Inasmuch as the synthesis of emodin could alone serve to distinguish between these formulæ, we have made numerous attempts to accomplish this by the condensation of hydroxysalicylic acid with the different hydroxytoluic acids under varying conditions of temperature and by the use of different condensing agents, such as zinc chloride and phosphoric anhydride, in addition to sulphuric acid. The desired condensation, however, did not take place, and it would appear that the hydroxysalicylic acid is so readily oxidised that it undergoes decomposition before the temperature necessary for condensation is reached.

In attempting the condensation of hydroxysalicylic with hydroxy-*p*-toluic acid ( $\text{CH}_3 : \text{OH} = 1 : 2$ ), it was found that a reaction had occurred, but the examination of the resulting products proved that they were formed by the condensation of two molecules of the hydroxy-*p*-toluic acid, and that the hydroxysalicylic acid took no part in the reaction. This was afterwards confirmed by the condensation of hydroxy-*p*-toluic acid alone. The formation of three, and only three, isomeric dihydroxydimethylantraquinones by the condensation of two molecules of hydroxy-*p*-toluic acid is possible, and three isomerides have actually been isolated. The formulæ of the isomerides are as follows :



The correct formulæ of the products were determined by the behaviour of these substances towards ammonia and methylating agents. On methylation, the substance denoted by formula III would yield a dimethyl ether, the compound No. II would furnish a mono-methyl ether, whilst the isomeride indicated by I would remain unchanged. The pure substances have been isolated and characterised.

#### EXPERIMENTAL.

*Emodin methyl ether*,  $\text{C}_6\text{H}_2(\text{OH})_2 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{CH}_3)(\text{OCH}_3)$ .

This compound was prepared as follows: 2.7 parts of emodin, 4.5 parts of methyl iodide, and 0.7 part of sodium dissolved in methyl alcohol were heated together in a reflux apparatus at  $60^\circ$  for 24 hours, or in



a sealed tube at  $100^{\circ}$  for 2 to 3 hours. The alcoholic liquid, which had now lost its original red colour, deposited yellow crystals, and these, when recrystallised from hot alcohol, separated in fine, yellow needles melting at  $200^{\circ}$ , the melting point remaining unchanged on further crystallisation. The ether was insoluble in sodium carbonate solution, but dissolved in cold aqueous sodium hydroxide to a red solution.

0.0864 gave 0.2134  $\text{CO}_2$  and 0.0346  $\text{H}_2\text{O}$ .  $\text{C} = 67.4$ ;  $\text{H} = 4.4$ .

0.0782 „ by Zeisel's method, 0.0638 AgI.  $\text{OCH}_3 = 5.2$ .

\* 0.2206 „ „ „ 0.185 AgI.  $\text{OCH}_3 = 5.3$ .

$\text{C}_{16}\text{H}_{12}\text{O}_5$  requires  $\text{C} = 67.6$ ;  $\text{H} = 4.2$ ;  $\text{OCH}_3 = 5.3$  per cent.

The *acetyl* compound,  $\text{C}_{16}\text{H}_{10}\text{O}_5(\text{C}_2\text{H}_3\text{O})_2$ , prepared by the action of acetic anhydride and sodium acetate, was purified by recrystallisation from hot alcohol until its melting point was constant at  $157^{\circ}$ .

0.1406 gave 0.3364  $\text{CO}_2$  and 0.0576  $\text{H}_2\text{O}$ .  $\text{C} = 65.2$ ;  $\text{H} = 4.5$ .

$\text{C}_{20}\text{H}_{16}\text{O}_7$  requires  $\text{C} = 65.2$ ;  $\text{H} = 4.3$  per cent.

When emodin methyl ether was fused with potassium hydroxide, a small quantity of phenol was produced, together with a small amount of an acid which sublimed forming light green crystals which did not melt below  $250^{\circ}$ , and developed purple and red colorations with ferric chloride and sulphuric acid respectively. Unfortunately, the quantity of this acid produced was too small to admit of further examination. It would appear that this emodin methyl ether is not identical with that obtained by Perkin and Hummel from *Ventilago madrasapatana* (Trans., 1894, 65, 932), since the acetyl compound of the latter melted at  $185^{\circ}$ , and the ether yielded crystalline mono- and tetra-nitro-compounds.

Under similar conditions, the ether prepared from emodin afforded no definite compound with nitric acid.

### 3 : 5-Dihydroxy-2 : 6-dimethylantraquinone, $\text{C}_{16}\text{H}_{12}\text{O}_4$ .

This was produced during an attempt to condense hydroxysalicylic with hydroxy-*p*-toluic acid ( $\text{CH}_3 : \text{OH} = 1 : 2$ ), but it was afterwards found that the former acid took no part in the condensation. *m*-Hydroxy-*p*-toluic acid, either alone or mixed with an equal part of hydroxysalicylic acid, was heated in an oil-bath at  $110^{\circ}$  to  $140^{\circ}$  for from 7 to 10 hours with ten parts of concentrated sulphuric acid. Whilst still warm, the deep red liquid was poured into ten volumes of water and allowed to cool. The dirty green precipitate produced was thoroughly washed with water, dried, and then extracted with benzene in a Soxhlet's apparatus. After removing the benzene by distillation, the

\* This specimen was obtained by the reaction at  $100^{\circ}$  in a sealed tube.

residue was dissolved in a large volume of hot glacial acetic acid, the solution being boiled with animal charcoal. The crystals, which separated on cooling from the filtered solution, did not melt below  $300^{\circ}$ ; they were crystallised twice from ethyl acetate and thus obtained as bright golden-yellow leaflets. The substance dissolved in concentrated sulphuric acid to a deep pink solution, and developed a brownish-red coloration in ammonia, a full red tint being produced in aqueous caustic alkalis; it is only slightly soluble in aqueous sodium carbonate, forming a reddish-yellow solution.

0.0854 gave 0.2224  $\text{CO}_2$  and 0.0344  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 4.5$ .

0.1164 „ 0.3030  $\text{CO}_2$  „ 0.0504  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 4.8$ .

$\text{C}_{16}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 71.6$ ;  $\text{H} = 4.5$  per cent.

The *acetyl* compound,  $\text{C}_{16}\text{H}_{10}\text{O}_4(\text{C}_2\text{H}_3\text{O})_2$ , prepared by the action of acetic anhydride and sodium acetate, formed long, yellow, acicular crystals melting at  $215^{\circ}$ , and this melting point was not altered on recrystallisation.

0.0842 gave 0.2102  $\text{CO}_2$  and 0.0372  $\text{H}_2\text{O}$ .  $\text{C} = 68.1$ ;  $\text{H} = 4.8$ .

$\text{C}_{20}\text{H}_{16}\text{O}_6$  requires  $\text{C} = 68.1$ ;  $\text{H} = 4.5$  per cent.

The *monomethyl ether*,  $\text{C}_{16}\text{H}_{11}\text{O}_4(\text{CH}_3)$ , was formed by heating the dihydroxydimethylantraquinone at  $100^{\circ}$  for 2 hours in a sealed tube with equivalent amounts of sodium and methyl iodide dissolved in methyl alcohol. The product, which separated on cooling, was collected, washed with water, and repeatedly crystallised from hot ethyl acetate, the ether being thus obtained in golden-yellow, acicular crystals melting at  $214\text{--}215^{\circ}$ .

0.093 gave, by Zeisel's method, 0.0702  $\text{AgI}$ .  $\text{OCH}_3 = 4.8$ .

$\text{C}_{17}\text{H}_{14}\text{O}_4$  requires  $\text{OCH}_3 = 5.3$  per cent.

A dimethyl ether could not be obtained.

The *acetyl* compound,  $\text{C}_{16}\text{H}_{10}\text{O}_4(\text{CH}_3)(\text{C}_2\text{H}_3\text{O})$ , prepared in the usual way with acetic anhydride and sodium acetate, when crystallised from absolute alcohol, formed light yellow, acicular crystals melting at  $195\text{--}196^{\circ}$ .

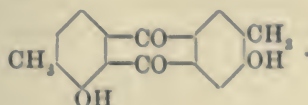
0.1012 gave 0.2580  $\text{CO}_2$  and 0.0440  $\text{H}_2\text{O}$ .  $\text{C} = 69.5$ ;  $\text{H} = 4.8$ .

0.0946 „ 0.2412  $\text{CO}_2$  „ 0.0428  $\text{H}_2\text{O}$ .  $\text{C} = 69.5$ ;  $\text{H} = 5.0$ .

$\text{C}_{19}\text{H}_{16}\text{O}_5$  requires  $\text{C} = 70.3$ ;  $\text{H} = 4.9$  per cent.

The formation of the monomethyl ether proves that the condensation product contains only one hydroxyl group contiguous to the carbonyl, and as of the three isomerides possible by the condensation of two molecules of *m*-hydroxy-*p*-toluic acid only one fulfils this con-

dition, it follows that the substance just described must be represented by the following formula :



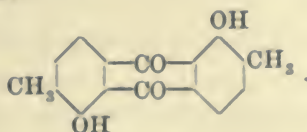
1 : 5-Dihydroxy-2 : 6-dimethylantraquinone,  $C_{16}H_{12}O_4$ .

This substance is formed together with the isomeric 3 : 5-dihydroxy-2 : 6-dimethylantraquinone under the conditions previously described (p. 1331). It is, however, only produced in very small quantity, and we have not obtained it by the condensation of hydroxy-*p*-toluic acid alone. It was isolated from the mother liquors, from which its isomeride had separated, by adding water to the glacial acetic acid solution. The product was purified by dissolving in hot chloroform, in which the yellow isomeride is almost insoluble, and precipitating from the chloroform solution by the cautious addition of methyl alcohol. After repeated crystallisation from chloroform and petroleum ether, the compound was obtained in scarlet, acicular crystals melting at  $224-225^\circ$ .

0.0732 gave 0.191  $CO_2$  and 0.0298  $H_2O$ .  $C = 71.2$  ;  $H = 4.5$ .

$C_{16}H_{12}O_4$  requires  $C = 71.6$  ;  $H = 4.5$  per cent.

The crystals were insoluble in ammonia or sodium carbonate solution, but dissolved in concentrated sulphuric acid to a purple solution, and developed a pink coloration with aqueous caustic alkalis. The substance remained unchanged when heated with excess of methyl iodide and sodium in methyl alcohol at  $100^\circ$  in a sealed tube. The insolubility of this isomeride in ammonia and its inertness towards methylating agents prove that both hydroxyl groups must be contiguous to carbonyl, and the compound must therefore be represented by the following formula :



3 : 7-Dihydroxy-2 : 6-dimethylantraquinone,  $C_{16}H_{12}O_4$ .

This substance is formed in very small proportion together with the isomeric 3 : 5-dihydroxy-2 : 6-dimethylantraquinone by the condensation of two molecules of *m*-hydroxy-*p*-toluic acid ; it was separated from the glacial acetic acid mother liquors by precipitation with water,

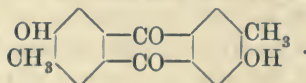


and crystallised repeatedly from absolute alcohol until of constant melting point. It then formed fine, orange-yellow, acicular crystals melting at  $232^{\circ}$ , was readily soluble in ammonia to a red solution, and developed a reddish-purple coloration in concentrated sulphuric acid.

0.0486 gave 0.1264  $\text{CO}_2$  and 0.021  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 4.8$ .

$\text{C}_{16}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 71.6$ ;  $\text{H} = 4.5$  per cent.

Although sufficient material was not available for any further experiments, yet the ready solubility of the substance in ammonia and its distinctive character leave no doubt but that this substance is the third possible isomeride, and therefore by exclusion has the following formula:



Emodin was fused with caustic alkali and oxidised with potassium permanganate under varying conditions, but in no case could any definite product be isolated.

An attempt to prepare a methyl ether of 5:8-dihydroxy-2-methyl-anthraquinone was unsuccessful. Further proof is thus afforded of the correctness of the generalisation that in derivatives of anthraquinone under the conditions mentioned, only those hydroxyl groups are capable of methylation which are not contiguous to either of the two carbonyl groups.

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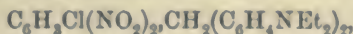
## CXXVIII.—*Additive Compounds of s-Trinitrobenzene and Alkylated Arylamines.*

By HAROLD HIBBERT and JOHN J. SUDBOROUGH.

IN a previous communication (Trans., 1901, 79, 522), it has been shown that *s*-trinitrobenzene, *s*-trinitrotoluene, and a number of other trinitro-derivatives readily form additive compounds with  $\alpha$ - or  $\beta$ -naphthylamine. These compounds are well-defined, relatively stable, crystalline substances, having a deep red or purple-black colour. They may be crystallised from various solvents, even glacial acetic acid, without being resolved into their components, but are all decomposed on boiling with dilute mineral acids. They readily yield sulphur-coloured acetyl derivatives, which are identical with the pro-

ducts obtained by the union of *s*-trinitrobenzene with the acetylated naphthylamines. In the present paper, we further show that they are capable of yielding benzoyl derivatives.

As early as 1882, Hepp (*Annalen*, 1882, 215, 344) described unstable additive compounds of aniline with trinitrobenzene, &c. Herz (*Ber.*, 1890, 23, 2540) mentions a compound of picryl chloride and diphenylamine which contains two molecules of the chloride united with one of the base. Herz also states that carbazole gives a similar compound with picryl chloride. Wedekind (*Annalen*, 1902, 323, 257) describes an additive compound of pyridine and picryl chloride containing 1 molecular proportion of each constituent. Paul Lemoult (*Compt. rend.*, 1902, 135, 346) has obtained additive compounds of 1-chloro-2:4-dinitrobenzene with bases of the diphenylmethane series; for example:  $C_6H_3Cl(NO_2)_2, CH_2(C_6H_4NMe_2)_2$  and



both in the form of reddish-brown needles. Picryl chloride and pieramide also combine with the same bases yielding black compounds. Bamberger and Müller (*Ber.*, 1900, 33, 102) mention additive compounds of picrylmethylnitrosoamine with  $\alpha$ - and  $\beta$ -naphthylamines of the type  $[(NO_2)_3C_6H_2 \cdot NMe \cdot NO]_3, C_{10}H_7 \cdot NH_2$ . Reitzenstein (*J. pr. Chem.*, 1903, [ii], 68, 252) describes additive compounds of 1-chloro-2:4-dinitrobenzene with various bases. Most of these additive compounds are relatively unstable, and thus differ from the naphthylamine derivatives previously described by one of us (*loc. cit.*).

No definite constitutional formulæ were ascribed to the compounds mentioned in the previous communication, although several possibilities were suggested. We are continuing the investigation of these additive products with the object of answering the following questions.

(1) Are secondary and tertiary bases of the naphthylamine series capable of forming additive compounds with *s*-trinitrobenzene, and, if such compounds are produced, in what important points do they differ from the additive compounds already described?

(2) What is the effect of introducing substituents into the trinitrobenzene molecule on the formation of additive compounds? We have already shown that *s*-trinitrobenzene and *s*-trinitrotoluene form these additive compounds, whereas *s*-trinitroxylenes and trinitromesitylenes do not. We hope to determine whether other substituents, for example, OMe, Br,  $NO_2$ , &c., have similar inhibiting effects.

(3) Is the property of forming additive compounds affected at all by the introduction of substituents into the arylamine; more especially do such substituents as bromine and the  $NO_2$  group, which tend to lessen the basic properties of the arylamine, also tend to destroy its power of forming additive products?

(4) Are polynitro-derivatives of other aromatic hydrocarbons, more especially naphthalene, also capable of uniting with arylamines, and, if so, do the products differ materially from those already described? So far, preliminary experiments have shown that tri- and tetra-nitro-naphthalenes are capable of forming additive compounds with  $\alpha$ - and  $\beta$ -naphthylamines. Certain of these contain one molecular proportion of the nitro-compound combined with one of the base, and in others, two molecules of the nitro-compound are united with one of the base.

The present paper gives an account of the work undertaken with the object of deciding the first of the foregoing questions. The fact that Hepp describes a compound of trinitrobenzene and dimethylaniline, and Wedekind one of pyridine and trinitrobenzene, indicates that certain tertiary bases are capable of forming these additive compounds.

We find that *s*-trinitrobenzene is capable of combining, not merely with primary arylamines of the type of the naphthylamines, but also with secondary and tertiary bases such as the mono- and di-alkylated naphthylamines, yielding well-defined compounds which, in appearance and stability, closely resemble those already described.

The products obtained from trinitrobenzene and mono-alkylated naphthylamines may be acetylated or benzoylated, whereas the corresponding derivatives of the tertiary bases may readily be crystallised from acetic anhydride without undergoing any alteration. We have also found that the compound obtained from trinitrobenzene and  $\alpha$ -naphthylamine may be benzoylated, and that the same compound, when heated with ethyl iodide and freshly ignited magnesia, yields a monoethyl derivative identical with that obtained by the addition of ethyl- $\alpha$ -naphthylamine to *s*-trinitrobenzene. At first, we considered that these facts pointed to the presence of a hydroxyl or an amidogen group in the additive compounds from naphthylamine and its monoalkyl derivatives and to the absence of any such radicles in the compounds from trinitrobenzene and dialkylated naphthylamines.

We had previously noticed, however, that when solutions of the coloured compounds were considerably diluted, the depth of colour diminished considerably, and determinations of the molecular weights of some of the additive compounds in moderately dilute benzene solution have proved that these substances are almost completely dissociated into their two components, even although the solution still retains an appreciable amount of colour. It appears probable, therefore, that the acylating and alkylating agents interact not with the additive compound itself as such, but with its basic constituent, and if this is a tertiary base (dimethylaniline, for example) no reaction occurs.



## EXPERIMENTAL.

A. *α*-Naphthylamine Derivatives.

1. *Ethyl-α-naphthylamine s-Trinitrobenzene*,  $C_{10}H_7 \cdot NHEt, C_6H_3(NO_2)_3$ .—Ethyl-*α*-naphthylamine was prepared by heating 100 grams of *α*-naphthylamine, 85 grams of ethyl bromide, and 220 grams of ethyl alcohol on the water-bath in a reflux apparatus for 7–8 hours. The crystals of the hydrobromide, which separated on cooling, were decomposed with aqueous potassium carbonate and the free base extracted with ether, the ethereal solution being repeatedly shaken with small amounts of dilute sulphuric acid in order to remove any unaltered primary base until no further precipitate of *α*-naphthylamine sulphate was obtained; the purified extract, after treatment with potassium carbonate solution, was dried and fractionated. Pure ethyl-*α*-naphthylamine, which was obtained as a pale yellow oil distilling at 301–302°, rapidly turned brown on exposure to light. The additive compound was prepared by mixing together warm benzene solutions of the two constituents in equivalent quantities; the dark red solution thus obtained deposited long, brick-red needles which were recrystallised from glacial acetic acid.

0·2008 gave 25 c.c. moist nitrogen at 15° and 766 mm.  $N = 14·71$ .

0·5047 „ 0·2870.  $C_6H_3(NO_2)_3 = 56·8$ .

$C_{18}H_{16}O_6N_4$  requires  $N = 14·58$  and  $C_6H_3(NO_2)_3 = 55·4$  per cent.

The compound melts at 153·5–154°,\* dissolves readily in benzene, acetone, glacial acetic acid, and hot alcohol; its molecular weight was determined by the cryoscopic method in benzene solution.

0·1070 in 18·4724 grams of solvent gave  $\Delta t$  0·140°.  $M = 202$ .

0·0899 „ 21·8892 „ „ „ „  $\Delta t$  0·1044°.  $M = 193$ .

$C_{18}H_{16}O_6N_4$  requires  $M = 384$ .

No definite acetyl derivative could be obtained. When the red compound was mixed with cold acetic anhydride, the characteristic colour gradually disappeared, and, on pouring the solution into water, a cream-coloured product was deposited, which, when crystallised from acetone, yielded trinitrobenzene. Attempts to prepare an acetyl derivative by the union of trinitrobenzene and *N*-ethylaceto-*α*-naphthalide also proved unsuccessful.

2. *Diethyl-α-naphthylamine s-Trinitrobenzene*,  $C_{10}H_7 \cdot NEt_2, C_6H_3(NO_2)_3$ .—Diethyl-*α*-naphthylamine, prepared by Morgan's method (Trans.,

\* All the melting points given in this communication were determined by the aid of short normal thermometers, the whole of the stem being immersed in the liquid.

1900, 77, 823) and freed from primary and secondary bases by distilling several times with small amounts of acetic anhydride, was obtained as a pale yellow oil distilling at 282—285° under atmospheric pressure; it did not show the same tendency to darken as the isomeric  $\beta$ -compound. The tertiary base was also prepared by heating  $\alpha$ -naphthylamine hydrochloride with ethyl alcohol (5—6 mols.) in sealed tubes at 250° for 24 hours.

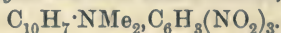
When hot benzene solutions containing molecular proportions of the tertiary base and trinitrobenzene were mixed, a deep red coloration was produced, but after a time the solution deposited a considerable amount of colourless trinitrobenzene. The additive compound was obtained by using a large excess of the base; it crystallises in long, scarlet needles, melts at 95—95·5°, may be crystallised from acetic anhydride without undergoing any change, and dissolves fairly readily in benzene, acetone, acetic acid, and hot alcohol.

0·2010 gave 23·8 c.c. moist nitrogen at 17° and 762 mm.  $N = 13·78$ .

0·5220 „ 0·2619.  $C_6H_3(NO_2)_3 = 50·17$ .

$C_{20}H_{20}O_6N_4$  requires  $N = 13·59$  and  $C_6H_3(NO_2)_3 = 51·7$  per cent.

### 3. *Dimethyl- $\alpha$ -naphthylamine s-Trinitrobenzene,*



—Dimethyl- $\alpha$ -naphthylamine, prepared by Friedländer and Welmann's method (*Ber.*, 1888, 21, 3124), was obtained as a colourless oil distilling at 271° under atmospheric pressure.

An almost theoretical yield of the additive compound was obtained by mixing together warm benzene solutions of the two constituents in molecular proportion; the product slowly separated in orange-red needles melting at 105—107°; it dissolved readily in acetic acid, benzene, or hot alcohol.

0·2534 gave 31·4 c.c. moist nitrogen at 14° and 763·5 mm.  $N = 14·65$ .

0·5268 „ 0·2908.  $C_6H_3(NO_2)_3 = 55·2$ .

0·5110 „ 0·2829.  $C_6H_3(NO_2)_3 = 55·3$ .

$C_{18}H_{16}O_6N_4$  requires  $N = 14·58$  and  $C_6H_3(NO_2)_3 = 55·4$  per cent.

The additive compound was quite stable in the presence of acetic anhydride, and after boiling with 4 parts of this reagent for 4—5 hours it separated again on cooling in crystals melting at 105—106°.

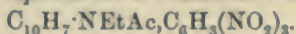
The molecular weight was determined by the cryoscopic method in acetic acid. 0·1363 gram in 13·13 grams of solvent gave  $\Delta t = 0·27^\circ$ ,  $M = 188·3$ .  $C_{18}H_{16}O_6N_4$  requires  $M = 384$ .

B.  $\beta$ -Naphthylamine Derivatives.

1. *Ethyl- $\beta$ -naphthylamine s-Trinitrobenzene*,  $C_{10}H_7 \cdot NHEt, C_6H_3(NO_2)_3$ .  
 —The ethyl- $\beta$ -naphthylamine, prepared by O. Fischer's method (*Ber.*, 1893, 26, 193), was obtained as a practically colourless oil distilling at  $232^\circ$  under 102 mm. pressure; it darkened on keeping. The additive compound was prepared in the usual manner by mixing benzene solutions containing molecular quantities of the two constituents. A deep bluish-red solution was thus obtained from which glistening, black, rhombic prisms were deposited. These melted at  $106^\circ$ , crystallised unchanged from acetic acid, and dissolved readily in most organic solvents.

0.1966 gave 24.4 c.c. moist nitrogen at  $15^\circ$  and 761 mm.  $N = 14.56$ .  
 0.5412 „ 0.3108.  $C_6H_3(NO_2)_3 = 57.4$ .

$C_{18}H_{16}O_6N_4$  requires  $N = 14.58$  and  $C_6H_3(NO_2)_3 = 55.4$  per cent.

2. *N-Ethylaceto- $\beta$ -naphthalide s-Trinitrobenzene*,

—Two grams of ethyl- $\beta$ -naphthylamine trinitrobenzene were shaken in the cold with excess of acetic anhydride for about 5–10 minutes. As soon as the characteristic red colour was completely destroyed, the mixture was poured into water and left for several hours; the yellow, crystalline solid was then collected and dried at the ordinary temperature and extracted with cold carbon disulphide. A small residue of colourless trinitrobenzene was obtained, and the solution, when allowed to evaporate at the ordinary temperature, deposited sulphur-yellow, glistening prisms melting at  $77$ – $78^\circ$ .

Extremely well-developed crystals were obtained when the crude product was dissolved in cold acetone and the solvent allowed to evaporate at the ordinary temperature.

0.2198 gave 25.0 c.c. moist nitrogen at  $12^\circ$  and 748.5 mm.  $N = 13.3$ .

$C_{20}H_{18}O_7N_4$  requires  $N = 13.14$  per cent.

The same compound was also obtained when acetone solutions of trinitrobenzene and *N*-ethylaceto- $\beta$ -naphthalide melting at  $50$ – $52^\circ$  were mixed and the solvent allowed to evaporate.

This acetyl derivative, unlike the other additive compounds, was found to be relatively unstable, and when dissolved in warm benzene or alcohol was resolved into its components, the solution, on cooling, depositing crystals of trinitrobenzene.

3. *Diethyl- $\beta$ -naphthylamine s-Trinitrobenzene*,  $C_{10}H_7 \cdot NEt_2, C_6H_3(NO_2)_3$ .

—The diethyl- $\beta$ -naphthylamine was obtained by Morgan's method as a practically colourless oil distilling at  $313^\circ$  under atmospheric pressure;



it rapidly turned brown and acquired a deep violet fluorescence. Black, lustrous prisms of the additive compound were obtained on mixing benzene solutions of the constituents in molecular proportions; the product crystallised unchanged from glacial acetic acid, melted at  $116^{\circ}$ , and dissolved readily in most organic solvents. Prolonged boiling with acetic anhydride did not decompose this additive compound, and it remained unchanged when subjected to the Schotten-Baumann reaction.

0.2305 gave 27.3 c.c. moist nitrogen at  $18^{\circ}$  and 762 mm.  $N = 13.7$ .

0.5214 „ 0.2612.  $C_6H_3(NO_2)_3 = 50.1$ .

$C_{20}H_{20}O_6N_4$  requires  $N = 13.6$  and  $C_6H_3(NO_2)_3 = 51.7$  per cent.

*Action of Methyl Alcoholic Potash on the Additive Compounds.*

It has been previously shown (Trans., 1901, 79, 528) that cold methyl alcoholic potash decomposes  $\alpha$ - and  $\beta$ -naphthylamine trinitrobenzenes, yielding Lobry de Bruyn's compound,



The action of the same reagent on dimethyl- $\alpha$ -naphthylamine and on diethyl- $\beta$ -naphthylamine trinitrobenzenes has also been investigated. The compounds were dissolved in benzene, the solutions cooled down to about  $-10^{\circ}$ , when part of the benzene solidified, and then the theoretical amount (1 mol.) of potassium hydroxide dissolved in pure methyl alcohol was slowly added.

At the low temperature, very little action occurred, but as the temperature rose a dark brown product was formed. This was removed when the temperature was about  $0^{\circ}$ , washed with methyl alcohol and benzene, and then dried and analysed. The percentage of potassium found in each case was 12.9. The product had all the properties of Lobry de Bruyn's compound, and it appears highly probable that these compounds of trinitrobenzene and tertiary bases are decomposed by methyl alcoholic potash in the same manner as the compounds of trinitrobenzene with the naphthylamines themselves.

*Benzo- $\alpha$ -naphthalide s-Trinitrobenzene,  $C_{10}H_7 \cdot NH \cdot CPh, C_6H_3(NO_2)_3$ .*

It has already been shown that  $\alpha$ -naphthylamine trinitrobenzene yields a monoacetyl, but not a diacetyl derivative (Trans., 1901, 79, 522); a monobenzoyl derivative has now been obtained by the aid of the Schotten-Baumann method; the product crystallises from carbon tetrachloride in brilliant, yellow needles melting at  $131-132^{\circ}$ .

The same compound was produced by mixing alcoholic solutions of trinitrobenzene and benzo- $\alpha$ -naphthalide.

0.2304 gave 23.8 c.c. moist nitrogen at 13.8° and 758.3 mm.  $N = 12.14$ .  
 $C_{23}H_{16}O_7N_4$  requires  $N = 12.17$  per cent.

*Action of Ethyl Iodide and Magnesia on  $\alpha$ -Naphthylamine s-Trinitrobenzene.*

Three grams of  $\alpha$ -naphthylamine trinitrobenzene, 1.8 grams of freshly ignited magnesia, and 30 grams of ethyl iodide were boiled for 16 hours in a reflux apparatus; the excess of ethyl iodide was removed by distillation and the residue extracted with hot alcohol. As the solution cooled, 1.2 grams of reddish-brown crystals melting at 147—153° were obtained, and a further quantity (1.4 grams) melting at about 145° separated from the mother liquor. The two fractions, when crystallised together from alcohol, yielded dark reddish-brown needles of ethyl- $\alpha$ -naphthylamine trinitrobenzene melting at 153°. So far it has not been found possible to obtain the diethyl compound by the alkylation of  $\alpha$ -naphthylamine trinitrobenzene in the presence of magnesia.

The results of similar experiments carried out according to the Purdie-Lander method of alkylation were not at all satisfactory, as the silver oxide appears to oxidise the basic part of the molecule, converting it into black, resinous substances.

*Compounds of Trinitrobenzene with Alkylated Anilines.*

The compounds formed by the union of trinitrobenzene and mono- and di-alkylated anilines (compare Hepp, *loc. cit.*) are somewhat difficult to prepare, as they readily decompose into their components when crystallised from the ordinary solvents. In all cases, it is necessary to employ a large excess of the base, as otherwise unaltered trinitrobenzene crystallises out. In some cases, the only practicable method of preparation is to dissolve the trinitrobenzene in an excess of the base and allow the additive compound to crystallise. The compounds of this series, when exposed to the air for some time, even at the ordinary temperature, give up the base and leave a practically colourless residue of trinitrobenzene.

The compounds we have prepared are:

(1) *Methylaniline s-trinitrobenzene*, dark red needles melting at 81—82°.

(2) *Dimethylaniline s-trinitrobenzene*, purple-black, prismatic needles melting at 108—109°.

(3) *Ethylaniline s-trinitrobenzene*, dark red needles melting at 55—56°.

(4) *Diethylaniline s-trinitrobenzene*, black prisms melting at 42—42·5°.

We wish to acknowledge our thanks to the Grant Committee of the Chemical Society for financial assistance, and to the firm of Messrs. Levinstein, Limited, for a gift of  $\alpha$ - and  $\beta$ -naphthylamines.

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### CXXIX.—*The Influence of Cyclic Radicles on Optical Activity: Tartaric ar- and ac-Tetrahydro- $\beta$ -naphthylamides, Furfurylamide, and Piperidide.*

By PERCY FARADAY FRANKLAND and ERNEST ORMEROD, M.Sc.

IN the extended investigation on the relative rotatory effect of different groups, on which one of us has been engaged for a number of years past, one of the methods of comparison employed has consisted in introducing the various radicles under examination into the amido-group of optically active amides (P. F. Frankland, Wharton, and H. Aston, *Trans.*, 1901, 79, 266).

The present communication deals with the rotatory influence of the partially reduced naphthalene rings, the furfuryl, and the piperidine groups; it includes a description of the preparation and properties of

- (1) Tartaric di-*ar*-tetrahydro- $\beta$ -naphthylamide.
- (2) „ di-*ac*-tetrahydro- $\beta$ -naphthylamide.
- (3) „ difurfurylamide.
- (4) „ dipiperidide.

The simpler substitution derivatives of tartramide form the subject of the succeeding communication.

The results of the present investigation are intimately connected with those recently recorded by Rupe in his comprehensive and important paper "Ueber den Einfluss der Kohlenstoffdoppelbindung auf das Drehungsvermögen optisch activer Substanzen" (*Annalen*, 1903, 327, 157), which only appeared after the greater part of our work had been completed.

In order to ascertain the relative rotatory effects of the aromatic and alicyclic rings, we have compared the rotations of tartaric  $\alpha$ -naphthyl-



amide,  $\beta$ -naphthylamide, *ar*-tetrahydro- $\beta$ -naphthylamide, and *ac*-tetrahydro- $\beta$ -naphthylamide, all of which were determined in pyridine solution with the following results :

|  | $[\text{M}]_D^{25}$ |   | $[\text{M}]_D^{25}$ |
|--|---------------------|---|---------------------|
| Tartaric di- $\alpha$ -naphthyl-<br>amide..... | + 400°              | Tartaric di- <i>ar</i> -tetrahydro-<br>$\beta$ -naphthylamide ..... | + 840°              |
| Tartaric di- $\beta$ -naphthyl-<br>amide.....  | + 1160              | Tartaric di- <i>ac</i> -tetrahydro-<br>$\beta$ -naphthylamide ..... | + 240               |

These figures show that the rotatory effect of the naphthalene nucleus varies greatly (*a*) according as it is attached to the aminic nitrogen by the  $\alpha$ - or the  $\beta$ -atom of carbon, and (*b*) according as to which benzene ring of the tetrahydronaphthalene nucleus is reduced.

It has been shown by Slator and one of us that the substituted tartramides containing aromatic radicles have much greater dextro-rotations than those containing fatty groups ; we should anticipate, therefore, that the *ar*-tetrahydro- $\beta$ -naphthylamide would have a rotation of the same order as  $\beta$ -naphthylamide, whilst that of the *ac*-tetrahydro- $\beta$ -naphthylamide should approximate to the rotation of tartramide substituted by fatty radicles. This is actually found to be the case, for the molecular rotation of tartaric *ar*-tetrahydro- $\beta$ -naphthylamide is less than that of  $\beta$ -naphthylamide itself, but greater than that of tartaric *p*-toluidide ( $[\text{M}]_D^{25} = +793^\circ$ ), whilst the molecular rotation of tartaric *ac*-tetrahydro- $\beta$ -naphthylamide is even less than that of either tartaric methylamide ( $[\text{M}]_D^{25} = +278^\circ$ ) or ethylamide, ( $[\text{M}]_D^{25} = +279^\circ$ ).

It has been shown by F. W. Aston and one of us (Trans., 1901, 79, 514) that the rotatory effect of the pyromucyl group is very similar to that of the benzoyl and toluyll groups, which implies that the rotatory effects of the furfuran and benzene rings must closely resemble each other ; it would be anticipated, therefore, that tartaric furfurylamide should possess a molecular rotation similar to that of the benzylamide. This was actually found to be the case, the rotations of the two being practically identical ; thus, in pyridine solution :

|                               | $[\text{M}]_D^{25}$ . |
|-------------------------------|-----------------------|
| Tartaric difurfurylamide..... | + 300—307°            |
| „ dibenzylamide .....         | + 300°                |

By way of commencing the study of optically active amides derivable from secondary amines, we have prepared tartaric dipiperidide, which proved to be practically inactive in a 3 per cent. solution of pyridine or aniline.

That a diminution in the molecular rotation should take place when both instead of only one atom of hydrogen in the NH group are

replaced was to be expected in view of Forster's results with the mono- and di-substituted bornylamines (Trans., 1899, 75, 936). It was, however, not to be anticipated from these results that the rotation of the piperidide would actually fall below that of tartramide itself.

The further investigation of this and similar amides is being continued by one of us.

### EXPERIMENTAL.

#### *Tartaric Di-ar-tetrahydro- $\beta$ -naphthylamide.*

The *ar*-tetrahydro- $\beta$ -naphthylamine was prepared by Clarence Smith's improvement (*Thesis, University of London, 1903*) on Bamberger's method (*Ber.*, 1890, 23, 882); a process which depends on the fractional crystallisation and subsequent hydrolysis of the acetyl derivative of the crude aromatic base obtained by the reduction of  $\beta$ -naphthylamine by means of sodium in amyl alcohol solution. The corresponding tartaric *ar*-tetrahydro- $\beta$ -naphthylamide was prepared by the action of the base on methyl tartrate as well as on free tartaric acid.

Methyl tartrate (1 mol.) and the aromatic base ( $2\frac{1}{4}$  mols.) were heated together for 5 hours in an oil-bath at  $140^\circ$ . The dark coloured product was extracted with alcohol, the solution boiled with animal charcoal, and filtered; the solid which separated on cooling, after being repeatedly crystallised from alcohol, melted sharply at  $186^\circ$  without decomposition.

0.2424 yielded 14.6 c.c. moist nitrogen at  $14^\circ$  and 746.5 mm.  $N = 6.96$ .

$C_{24}H_{28}O_4N_2$  requires  $N = 6.86$  per cent.

The substance readily crystallises in colourless, clustered needles from either absolute or dilute alcohol; it is moderately soluble in cold alcohol and more so in the hot solvent. Although insoluble in water, it dissolves in benzene, toluene, ethyl acetate, glacial acetic acid, and is extremely soluble in pyridine.

The following polarimetric results were obtained:

#### *Rotation of Tartaric Di-ar-tetrahydro- $\beta$ -naphthylamide.* (Prepared from methyl tartrate.)

Pyridine solution. Temp. =  $20^\circ$ . Length of tube = 199.89 mm.

| Per cent.<br>solution = $p$ . | $d\ 20^\circ/4^\circ$ . | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------------------------------|-------------------------|-------------------------|---------------------------|----------------------|
| 1.379                         | 0.9810                  | + 5.50°                 | + 203.4°                  | + 830°               |
| 3.255                         | 0.9868                  | 13.13                   | 204.5                     | 834                  |
| 3.300                         | 0.9872                  | 13.38                   | 205.5                     | 838                  |
| 4.427                         | 0.9897                  | 18.03                   | 205.9                     | 840                  |

The substance was also prepared by heating free tartaric acid (1 mol.) with the base (2 mols.) in an oil-bath at 130—140° for 6 hours; the further treatment was exactly similar to that described above; the crystals obtained also melted at 186°.

A pyridine solution gave the following polarimetric results :

| $\rho$ . | $d\ 20^{\circ}/4^{\circ}$ . | $\alpha_D^{20}$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|----------|-----------------------------|-------------------|---------------------|----------------|
| 2.517    | 0.9841                      | +10.07°           | +203.4°             | +830°          |

Thus the products obtained by the two different methods of preparation gave practically identical results, affording strong presumptive evidence against any racemisation having taken place.

#### *Tartaric Di-ac-tetrahydro- $\beta$ -naphthylamide.*

The *ac*-tetrahydro- $\beta$ -naphthylamine was prepared by Bamberger's method (*Ber.*, 1888, 21, 850).

After numerous trials, the following process was found to be the most satisfactory for the preparation of the amide. Ethyl tartrate (1 mol.) and *ac*-tetrahydro- $\beta$ -naphthylamine (2½ mols.) were heated together in an oil-bath for 12 hours at 140—145°. On cooling, the mixture solidified to a brown, brittle mass, which was powdered and boiled with very dilute hydrochloric acid in order to remove any unaltered base. The alcoholic solution of the residue was heated with animal charcoal for 2 days, then filtered and poured into water, the yellow, amorphous precipitate being dried and digested with ether free from alcohol. This treatment removed almost the whole of the remaining colouring matter, and the powder, which was now almost white, was crystallised 6 or 7 times from alcohol, and then from a mixture of alcohol and pyridine. Finally, it was extracted with cold pyridine, which dissolved almost the whole and left only a small quantity of substance melting at 255—260°. The pyridine solution was evaporated and the residue recrystallised from alcohol.

The substance so obtained is a white, micro-crystalline solid melting at 221° without decomposition. It is insoluble in water, ether, and benzene, slightly soluble in boiling alcohol, and moderately so in pyridine.

0.1342 yielded 7.95 c.c. moist nitrogen at 12° and 764 mm.  $N = 7.07$ .

$C_{24}H_{28}O_4N_2$  requires  $N = 6.86$  per cent.



*Rotation of Tartaric Di-ac-tetrahydro- $\beta$ -naphthylamide.*  
(Prepared from ethyl tartrate).

Pyridine solution. Temp. = 20°. Length of tube = 199.89 mm.

| Per cent.<br>solution = $p$ . | $d$ 20°/4°. | $\alpha_D^{20}$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|-------------------------------|-------------|-------------------|---------------------|----------------|
| 0.951                         | 0.981       | + 1.08°           | + 57.9°             | + 236°         |
| 1.996                         | 0.983       | 2.31              | 58.9                | 240            |
| 2.173                         | 0.986       | 2.50              | 58.4                | 238            |

The tartaric di-ac-tetrahydro- $\beta$ -naphthylamide was also prepared by heating together tartaric acid (1 mol.) and the alicyclic base ( $2\frac{1}{4}$  mols.) in an oil bath at 160° for 10—12 hours. The amide was extracted in the manner described above, but the yield was much inferior; the purified product melted at 220—221° and exhibited the following rotation in pyridine solution :

| $p$ . | $d$ 20°/4°. | $\alpha_D^{20}$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|-------|-------------|-------------------|---------------------|----------------|
| 1.881 | 0.983       | + 2.19°           | + 59.1°             | + 241°         |

The products obtained by both methods of preparation had thus practically the same rotation.

*Tartaric Difurfurylamide.*

The furfurylamine was prepared by the reduction of furfuraldoxime with sodium amalgam in alcoholic solution in the presence of acetic acid (Goldschmidt, *Ber.*, 1887, 20, 730).

Furfuraldoxime was first prepared by Odernheimer (*Ber.*, 1883, 16, 2988), by the interaction of furfuraldehyde and hydroxylamine at a moderate temperature, as a substance crystallising from ligroin in needles melting at 45—46°, but on boiling its alcoholic solution with hydroxylamine hydrochloride, the melting point is raised to 89°. Goldschmidt (*loc. cit.*) obtained the aldoxime of melting point 89° directly by boiling an alcoholic solution of furfural with free hydroxylamine for one hour.

Goldschmidt and Zanoli (*Ber.*, 1892, 25, 2573) have further shown that the compound melting at 89° is the *syn*-furfuraldoxime, that the *anti*-aldoxime melts at 73—74°, and that the product melting at 45—46° is a mixture of the two.

On employing Goldschmidt's method, however, we always obtained a beautifully crystalline product melting at 60—70°, even after 6 or 7 crystallisations from ligroin, and thus showing that both *syn*- and *anti*-aldoximes were still present. On treating this product, however, with hydrochloric acid, decomposing the resulting hydrochloride with

caustic soda, and then crystallising from ligroin, the *syn*-aldoxime was obtained with a sharp melting point of  $89^{\circ}$ , the *anti*-aldoxime having been converted into the *syn*-compound in the process.

Ultimately we adopted the following method of preparation: furfuraldehyde (1 mol.) was heated with an alcoholic solution of free hydroxylamine ( $1\frac{1}{2}$  mols.) on the water-bath for 2—3 hours, after which the alcohol was evaporated and the black residue extracted several times with boiling ligroin. The crystals deposited from the ligroin extract were twice distilled under reduced pressure, with a view to converting any *anti*- into *syn*-aldoxime, and, after recrystallising from ligroin, the pure *syn*-furfuraldoxime was at once obtained, melting at  $89^{\circ}$ .

The *syn*-furfuraldoxime was reduced to the amine by the method indicated by Goldschmidt: 15 grams of the oxime were dissolved in 300 grams of absolute alcohol, and 700 grams of  $2\frac{1}{2}$  per cent. sodium amalgam were added in small quantities at a time, the liquid being kept acid by the addition of glacial acetic acid, of which altogether about 60 grams were required, whilst the temperature was throughout maintained at  $25$ — $30^{\circ}$ . The reduction being complete, water was added and most of the alcohol driven off on the water-bath; the residual liquid was then extracted with ether to remove some resinous matter, caustic soda being added to set free the amine, which was then extracted with ether. The ethereal solution was dried and the furfurylamine fractionated; the yield was 40 per cent. of the theoretical.

The tartaric difurfurylamide was prepared as usual both by action of the amine on the ester as well as on free tartaric acid.

Ethyl tartrate (1 mol.) and furfurylamine ( $2\frac{1}{2}$  mols.) were heated together for 6 hours at  $130$ — $140^{\circ}$  in an oil-bath. The dark-coloured residue was boiled with water and filtered. The crystals, which separated on cooling the filtrate, were collected, dissolved in water, and the solution boiled with animal charcoal until colourless. The product crystallising from the colourless solution was further crystallised several times from water. The tartaric difurfurylamide thus obtained separated in beautiful, colourless plates melting sharply at  $179^{\circ}$ ; it is easily soluble in hot, but only slightly in cold water, very easily soluble in pyridine, and moderately so in alcohol and in ethyl acetate. The amide readily dissolves in cold aqueous caustic potash, being reprecipitated on the addition of acids, but when boiled with caustic potash solution or with hydrochloric acid it is rapidly hydrolysed with the formation of tartaric acid and furfurylamine.

0.2408 yielded 18.2 c.c. moist nitrogen at  $14^{\circ}$  and 758 mm.  $N = 8.87$ .

$C_{14}H_{16}O_6N_2$  requires  $N = 9.09$  per cent.

The following polarimetric results were obtained in pyridine solution :

*Rotation of tartaric difurfurylamide* (prepared from ethyl tartrate). Temp. 20°. Length of tube = 199.89 mm.

| Per cent.<br>solution = $p$ . | $d$ 20°/4°. | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------------------------------|-------------|-------------------------|---------------------------|----------------------|
| 0.9182                        | 0.980       | + 1.75°                 | + 97.3°                   | + 300°               |
| 3.013                         | 0.988       | 5.85                    | 98.3                      | 303                  |
| 4.883                         | 0.992       | 9.62                    | 99.4                      | 306                  |

The tartaric difurfurylamide was also prepared by heating together finely powdered tartaric acid (1 mol.) and furfurylamine ( $2\frac{1}{2}$  mols.) for 6 hours at 140—150° in an oil-bath. The resulting black mass was dealt with in the manner described in the foregoing preparation, a similar product melting at 178—180° being obtained; the yield was, however, much less satisfactory. This preparation gave the following polarimetric results in pyridine solution :

| $p$ . | $d$ 20°/4°. | $\alpha_D^{20^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------|-------------|-------------------------|---------------------------|----------------------|
| 1.136 | 0.981       | + 2.17°                 | + 97.4°                   | + 300°               |
| 3.806 | 0.9898      | 7.50                    | 99.6                      | 307                  |

Identical rotations were thus obtained with the furfurylamide prepared by the two different methods.

*Tartaric Dipiperidide*—Ethyl tartrate (1 mol.) and piperidine ( $2\frac{1}{2}$  mols.) were heated together for 5 hours at 140—150° in an oil-bath. On cooling, the mass became very viscid, and yielded crystals when left overnight. The unchanged piperidine was extracted with a little water; the crystals were collected, dissolved in benzene, and the solution boiled with animal charcoal until colourless. After a few crystallisations from benzene, very fine, small, colourless needles were obtained melting at 189—190°; these were moderately soluble in hot, but only slightly in cold water, soluble also in alcohol and in pyridine.

0.1696 yielded 14.5 c.c. moist nitrogen at 11° and 753 mm.  $N = 10.1$ .

$C_{14}H_{24}O_4N_2$  requires  $N = 9.8$  per cent.

A 3 per cent. solution in pyridine, even when examined in a 200 mm. tube, was found to be almost inactive, as was also a solution of similar strength in aniline.

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### CXXX.—*The Influence of Various Substituents on the Optical Activity of Tartramide.*

By PERCY FARADAY FRANKLAND and ARTHUR SLATOR, M.Sc., Ph.D.

THIS research forms a part of the systematic investigation which is being carried out by one of us on the rotatory power of optically active amides and their substitution products (see P. F. Frankland, F. M. Wharton, and H. Aston, *Trans.*, 1901, 79, 266).

In this part of the investigation, various substituted amides,  $(\text{CH}\cdot\text{OH})_2(\text{CONHR})_2$  of tartaric acid have been prepared and their rotation observed in solution, the primary object being to ascertain the influence on optical rotation of the various radicles *R*. Some of these amides have been prepared before, but with the exception of the toluidides and anilide their rotations have not been determined.

P. A. Guye and A. Babel (*Arch. Sci. phys. nat.*, 1899, [iv], 7, 34) have published determinations of the anilide and toluidides in pyridine solutions of 5 per cent. concentration, but the figures given differ considerably from those recorded in this paper, and these discrepancies are discussed later (p. 1352). The following is the general method of preparation: the amine (2 mols.) is heated with tartaric acid or methyl tartrate (1 mol.) either directly or in alcoholic solution. The yields are good, and the resulting amides are purified by crystallisation from a suitable solvent until the melting point is constant. In general, the amides are white, somewhat insoluble substances, usually crystallising in needles or flat plates; they melt at high temperatures, undergoing more or less decomposition.

The methyl ester was obtained by the method of preparation described by P. F. Frankland and F. W. Aston (*Trans.*, 1901, 79, 517); when distilled *in vacuo* and crystallised from benzene and ligroin, it had a rotation  $\alpha_D^{100} = +7.79^\circ$ .

The aromatic amides, which were only slightly soluble in the commoner solvents at the ordinary temperature, dissolved fairly readily in cold pyridine. The amide and the hydrazide were the only two derivatives which were practically insoluble in pyridine, and their rotations were determined in aqueous solution.

The compounds were recrystallised until they were optically constant, and the rotations were then determined at various concentrations by means of a Laurent half-shadow polarimeter. The length of the tube was usually 100 mm. for strong solutions and 300 mm. for dilute solutions; the tube was surrounded by a water-jacket with an arrangement for obtaining a constant temperature, and the rotations, except where otherwise stated, were determined at  $20^\circ$ .

The pyridine used for the rotation was Kahlbaum's "gereinigt," which was dried with lime or caustic potash and distilled. This base is a remarkably good solvent for many organic substances and, as has been shown (W. R. Innes, Trans., 1901, 79, 261) by ebullioscopic observations, the compounds are not associated in solution. The molecular weight of tartaric *p*-toluidide as determined by the rise in boiling point of pyridine solutions was 331, 330, and 354 with concentrations of 1.23, 2.42, and 3.67 grams per 100 grams of the solvent, the normal molecular weight being 328.

Pyridine is a strongly dissociating solvent as compared with other organic liquids, and its effect on the specific rotation of optically active substances at various concentrations has not hitherto been determined. It will be seen that for low concentrations the specific rotation is in most cases constant. Ethyl tartrate in pyridine solution (now being examined by one of us) gives a specific rotation which is almost constant up to 10 per cent. This constant is about 8 times as large as the specific rotation of the pure ester, and also several times larger than that determined in any other solvent (alcohol, water, &c.), even at the highest dilution. In the case of the amides, again, it is noticeable that water and alcoholic solutions generally give lower rotations than pyridine solutions.

Most of the amides of *d*-tartaric acid have very high positive rotations, and the appended list (p. 1367) gives a comparison of their molecular rotations. Tartramide has a positive molecular rotation of nearly 160° in water solution and about 210° in methyl alcohol solution. With the exception of the phenylhydrazide, the substituted amides hitherto examined have a higher molecular rotation. Aromatic groups (such as toluidide, anilide, naphthylamide) raise the rotation very considerably, whereas the effect of the aliphatic radicles (such as ethylamide and methylamide) is smaller.

The dextro-influence of the anilide and toluidide groups is as follows: *p*-toluidide > *m*-toluidide > anilide > *o*-toluidide. The *o*-toluidide is considerably lower than the others. It is noticeable that in the substitution of hydroxy-groups by benzoyl and the three toluy groups it has been found that the dextro-influence is in the order *p*-toluy > *m*-toluy > *o*-toluy, whilst the relative position of the benzoyl group varies in different substances (P. F. Frankland, Trans., 1899, 75, 345). The same order is noticed in the isomeric toluidides as given above, whilst the *m*-toluidide and anilide have almost identical molecular rotations.

The  $\beta$ -naphthylamide has a much higher rotation than the  $\alpha$ -compound. There is a resemblance in constitution between an  $\alpha$ - and an ortho-compound, and also between a  $\beta$ - and either a para- or a meta-compound, and this similarity is brought out in the rotation of these



amides. Thus the  $\alpha$ -naphthylamide is more soluble, has a lower melting point, and a lower rotation than its  $\beta$ -isomeride, and, similarly, the *o*-toluidide is more soluble, has a lower melting point and a lower rotation than the para-compound.

The ethylamide and methylamide have almost identical molecular rotations in pyridine, but in water the former has a slightly higher rotation. The influence of these two groups is in the positive direction, but is not nearly so great as that of the aromatic groups previously discussed above.

Tartaric hydrazide has a slightly higher molecular rotation than tartramide; the phenylhydrazide, however, unexpectedly exhibits a much lower rotation than either of the former compounds, but, on the other hand, the hydrazones have extremely high rotations, thus:

|                                 |  | $[\text{M}]_D^{20}$ . |
|---------------------------------|--|-----------------------|
| Tartramide .....                | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}_2 \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{NH}_2 \end{array}$ .....   | +158°                 |
| Tartaric hydrazide .....        | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}\cdot\text{NH}_2 \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{NH}_2 \end{array}$ .....   | 170                   |
| Tartaric phenylhydrazide .....  | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 \end{array}$ .....   | <80                   |
| Tartaric benzylidenehydrazone . | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_5 \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_5 \end{array}$ .   | 554                   |
| Tartaric furfurylidenehydrazone | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_4\text{H}_3\text{O} \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_4\text{H}_3\text{O} \end{array}$   | 736                   |
| Tartaric acetophenonehydrazone  | $\begin{array}{c} \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{C} \begin{array}{l} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} \\   \\ \text{---C---CO}\cdot\text{NH}\cdot\text{N}:\text{C} \begin{array}{l} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array} \end{array}$ | 397                   |

The great influence on the rotation brought about by the introduction of the benzylidene, furfurylidene, and acetophenone residues respectively is doubtless an example of the phenomenon which has recently been attracting much attention, namely, the powerful rotatory effect of a double linking, either between two carbon atoms or between an atom of carbon and an atom of nitrogen (Eykmann, *Ber.*, 1891, 24, 1278; Binz, *Zeit. physikal. Chem.*, 1893, 12, 723; Forster, *Trans.*, 1899, 75, 1149; Walden, *Zeit. physikal. Chem.*, 1896, 20, 569; Haller and Müller, *Compt. rend.*, 1899, 128, 1270; 129, 1005; Haller and Minguin, *Compt. rend.*, 1900, 130, 362; Rupe, *Annalen*, 1903, 327, 157; *Ber.*, 1903, 36, 2796; Haller, *Compt. rend.*, 1906, 1222).

It is worthy of note that the tartaric hydrazones may be capable of existing in two (or even three) geometrically isomeric forms, and, as these isomerides would doubtless differ considerably in rotation, it is obvious that a strict comparison of the rotations observed is hardly warrantable until these compounds have been more fully investigated from this point of view.



In order to ascertain the influence of a benzene ring united through a side chain, the benzylamide of tartaric acid has been prepared. It is interesting to note that this amide ranks with the fatty amides and has a molecular rotation slightly higher than the methyl- and ethyl-amides, and not nearly so high as the aromatic amides, thus confirming the rule previously enunciated with respect to distance from the asymmetric carbon atom. This was also previously found to be the case in the substitution of hydroxyl radicles, in which the phenacetyl group ranks rather with the aliphatic radicles than with the aromatic ones. Thus we have a uniform resemblance between acetyl, phenacetyl, benzoyl, and toluyll groups, replacing the hydrogen of the hydroxyl group, and the ethylamide, benzylamide, anilide, toluidide, and other groups replacing the hydroxyls of the carboxyl groups.

As already mentioned, the rotations of the anilide and toluidides observed by Guye and Babel differed considerably from the values obtained in the present communication. Our results were verified by observations of the rotatory power of specimens of the anilide and toluidides prepared from the ester of tartaric acid and the corresponding aromatic amine. Fresh preparations of these amides, made by Miss M. B. Thomas, afforded a further confirmation of our results.

The following table gives a comparison of the different values\* obtained:

*Rotations in Pyridine Solutions.*

| Amide.                    | $[\alpha]_D^{20^\circ}$ |              | $[\alpha]_D^{15^\circ}$ |       |
|---------------------------|-------------------------|--------------|-------------------------|-------|
|                           | Slator.                 | Miss Thomas. | Miss Thomas.            | Guye. |
| Anilide .....             | 246                     | 246          | 249                     | 259   |
| <i>p</i> -Toluidide ..... | 242                     | 241          | 243                     | 240   |
| <i>o</i> - „ .....        | 199                     | 203          | 205                     | 239   |
| <i>m</i> - „ .....        | 224                     | 226          | 228                     | 233   |
| „ „ .....                 | 218                     |              |                         |       |

The first specimen of the *m*-toluidide was prepared from Kahlbaum's *m*-toluidine, the second from König's specially pure base. It is remarkable that the density of Guye and Babel's 5 per cent. solutions (about 0.966) is so considerably smaller than that determined by Miss Thomas and ourselves (about 0.994), and even smaller than that of pure pyridine itself (about 0.980).

By correcting for the manifestly erroneous density of the pyridine solutions given by Guye and Babel, their rotations for the anilide and *m*-toluidide become practically the same as ours, whereas their rota-

\* These values are independent of the concentration of the solutions.

tions for the ortho-compound are materially higher, and for the para-isomeride lower, than our own observations for the corresponding compounds.

Besides the amides described, two of the imide compounds have been prepared, namely, tartranil and tartaric *p*-toluil. Estimations of the rotations have been taken in pyridine and methyl alcohol solutions. As we should expect, the toluil has a higher rotation than the anil, although they are not so high as the corresponding toluidide and anilide.

Ladenburg (*Ber.*, 1896, 29, 2710) describes two imides, namely methyl and ethyl tartrimide, which have respectively molecular rotations of  $+281^\circ$  and  $+261^\circ$  in 7.3 per cent. aqueous solution.

In these cases, the imide compound has a slightly higher molecular rotation than the corresponding amides in aqueous solution, but, inasmuch as the ethylimide has a lower molecular rotation than the methylimide, it suggests that with aromatic radicles the rotation should be still lower, as with tartranil in aqueous solution we have actually found to be the case.

Walden (*Zeit. physikal. Chem.*, 1895, 17, 248) similarly found malanil and malic  $\beta$ -naphthimide to have lower rotations than the amides. The comparatively low rotation of all these imides is remarkable in view of the fact that they contain a cyclic grouping, which is generally attended with a high rotation.

If only one series of compounds, the amides, for example, be prepared from tartaric acid, only the comparative rotatory influences of the various amide groups in the molecule will be obtained. Similarly, by preparing amides of acetyltartaric acid, another series is obtained, and it will be possible to judge whether the acetyl group has in any way a constant influence and whether the amide groups have the same comparative influences as in the foregoing series. So far, we have only one acetyl derivative, the rotatory power of which has been determined. Others have been prepared, but their rotations are as yet unknown. The *o*-toluidide of acetyltartaric acid, which has been prepared by acetylating the *o*-toluidide, gives a lower molecular rotation than any of the other compounds described in this paper excepting the phenylhydrazide.

The diminution in rotation which we have observed on acetylating tartaric *o*-toluidide is what would be anticipated from the known relationship between the rotations of the tartaric esters and their diacetyl derivatives.

Similarly, inasmuch as it has been shown by Purdie and Irvine (*Trans.*, 1901, 79, 957) that the dextro-rotation of the tartaric esters is enhanced by replacing the  $>\text{CH}\cdot\text{OH}$  groups by  $>\text{CH}\cdot\text{OMe}$ , we should anticipate that the dextro-rotation of tartramide would be

exceeded by that of dimethoxysuccinamide, and this is actually found to be the case. A survey of these relations is conveniently obtained by means of the following data:

|  | $[M]_D^{20^\circ}$ |  | $[M]_D^{20^\circ}$ |
|--|--------------------|--|--------------------|
| Ethyl dimethoxysuccinate (liquid) .....    | + 210.6°           | Ethyl diacetyltartrate (liquid) .....                    | + 9.9°             |
| Dimethoxysuccinamide (aqueous solution)... | 166.2              | Tartaric <i>o</i> -toluidide (pyridine solution) ...     | + 667.0            |
| Tartramide (aqueous solution).....         | 158.0              | Diacetyltartaric <i>o</i> -toluidide (pyridine solution) | + 80.0             |
| Ethyl tartrate (liquid)                    | 15.8               |  |                    |

### EXPERIMENTAL.

#### *Tartramide.*

This substance slowly crystallised in well-defined needles from a methyl alcoholic solution of methyl tartrate which had been saturated with dry ammonia at the temperature of a mixture of ice and salt, a further crop of crystals being obtained by removing ammonia from the mother liquor in a vacuum desiccator. The amide melted at 195° with decomposition.

0.1307 gave 21.3 c.c. moist nitrogen at 20.3° and 759.7 mm.  $N = 18.63$ .

$C_4H_8O_4N_2$  requires  $N = 18.92$  per cent.

Tartramide is insoluble in chloroform, benzene, ligroin, acetone, ether, and cold pyridine; it is slightly soluble in alcohol and dissolves more readily in water. At 12°, 100 grams of methyl, ethyl, and isobutyl alcohols dissolve respectively 0.1987, 0.0355, and 0.0152 gram of tartramide.

Rotations were taken in aqueous and in methyl alcohol solutions, but owing to the insolubility of the substance very dilute solutions had to be used. The rotation in aqueous solution remained unaltered after 31 days, and on heating the solution from 14—30° no variation in rotation was observed;  $[\alpha]_D$  at 14°, 20°, and 30° was found to have the values +107°, 106°, 107°, respectively.

#### *Rotations in Water.*

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d_{20^\circ/4^\circ}$ . | $[\alpha]_D^{30^\circ}$ . | $[M]_D^{30^\circ}$ . |
|-------------------------------|------------------------------|-------------------------------------|---------------------------|----------------------|
| 1.305                         | + 1.394°                     | 1.0031                              | + 106.5°                  | + 158°               |
| 0.077                         | 0.083                        | 0.9984                              | 108                       | 160                  |



### Rotations in Methyl Alcohol.

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|----------------------------|------------------------|------------------------------------|---------------------|----------------|
| 0.1797                     | 0.207°                 | 0.7997                             | +144°               | 213°           |
| 0.0807                     | 0.090                  | 0.7930                             | 141                 | 208            |

### Tartranilide (Polikier, *Ber.*, 1891, 24, 2959).

This compound was prepared by slowly adding 1 part of dry tartaric acid to 5 parts by weight of boiling aniline.

A white mass (aniline hydrogen tartrate) at first separated, but soon redissolved, and when all the tartaric acid had been added the contents of the flask suddenly solidified to a mass of yellowish-white, pearly plates. These crystals, which were rendered colourless by washing successively with dilute hydrochloric acid and a small quantity of alcohol, were found to be insoluble in water, only very slightly soluble in benzene, ligroin, chloroform, glacial acetic acid, and nitrobenzene, but dissolving readily in cold pyridine; when recrystallised from methyl alcohol, they melted at 250° with decomposition.

- 0.2003 gave 16.7 c.c. moist nitrogen at 21° and 746.9 mm.  $N = 9.32$ .
  - 0.2012 „ 0.1001  $H_2O$  and 0.4725  $CO_2$ .  $C = 64.06$ ;  $H = 5.53$ .
  - 0.2002 „ 0.0994  $H_2O$  „ 0.4691  $CO_2$ .  $C = 63.90$ ;  $H = 5.52$ .
- $C_{16}H_{16}O_4N_2$  requires  $N = 9.33$ ;  $C = 64.00$ ;  $H = 5.33$  per cent.

### Rotations in Pyridine.

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|----------------------------|------------------------|------------------------------------|---------------------|----------------|
| 5.421                      | +13.26°                | 0.9920                             | +246.5°             | +740°          |
| 1.820                      | 4.39                   | 0.9825                             | 245.6               | 737            |

This anilide was also prepared from methyl tartrate and aniline, and was purified by crystallisation from alcohol. This specimen gave the following data:  $p = 3.100$ ;  $\alpha_D^{20}(l=1) = +7.535^\circ$ ;  $d_{20}^{20}/4^\circ = 0.9854$ ;  $[\alpha]_D^{20} = +246.7^\circ$ ;  $[M]_D^{20} = +740^\circ$ .

These results were confirmed by rotations obtained from another specimen made from the acid.\* Traces of water in the pyridine solution were found to affect the rotation appreciably (to 3 or 4 per cent.), and the following results were obtained from the specially dried solvent:

\* This specimen was independently prepared and examined by Miss M. B. Thomas.

| Per cent.<br>solution = $p$ . | $\alpha_D(l=1)$ . | Density<br>$d\ 20^\circ/4^\circ$ | $[\alpha]_D$ . | $[M]_D$ . |
|-------------------------------|-------------------|----------------------------------|----------------|-----------|
| At $20^\circ$ { 2.289         | +5.54°            | 0.9847                           | +245.9°        | 738°      |
| { 4.05                        | 9.86              | 0.9877                           | 246.4          | 739       |
|                               |                   | $d\ 15^\circ/4^\circ$ .          |                |           |
| At $15^\circ$ 4.05            | 10.03             | 0.9936                           | 249.3          | 748       |

The rotation diminishes slightly with increase of temperature, as shown by the above numbers.

*Rotation in Methyl Alcohol.*— $p=0.0803$ ;  $\alpha_D^{20^\circ}(l=1) = +0.127^\circ$ ;  $d\ 20^\circ/4^\circ = 0.792$ ;  $[\alpha]_D^{20^\circ} = +200^\circ$ ;  $[M]_D^{20^\circ} = +600^\circ$ .

*Tartaric p-Toluidide,  $(C_7H_7 \cdot NH \cdot CO)_2 \cdot (CH \cdot OH)_2$ .*

This substance can be prepared by heating *p*-toluidine hydrogen tartrate (1 mol.) with toluidine (1 mol.) (Bischoff, *Ber.*, 1890, 23, 2049), but is more readily obtained by heating *p*-toluidine (2 mols.) and tartaric acid (1 mol.) for about 10 hours in an oil-bath at  $180$ — $185^\circ$ . The mixture of reagents did not fuse and the reaction was rather slow.

The *p*-toluidide, which remained after extracting the product successively with boiling water, dilute hydrochloric acid, and alcohol, was crystallised from a mixture of alcohol and pyridine and then melted at about  $240^\circ$  with decomposition. This substance is slightly soluble in ethyl and methyl alcohols, and still less so in chloroform, acetone, carbon disulphide, and water; it dissolves in hot aniline, hot nitrobenzene, strong sulphuric acid (without blackening), and also in pyridine.

0.2863 yielded 21.0 c.c. moist nitrogen at  $14.6^\circ$  and 751 mm.  $N = 8.51$ .

$C_{18}H_{20}O_4N_2$  requires 8.56 per cent.

*Rotations in Pyridine.*

The first preparation, which had possibly slightly racemised, gave a constant rotation  $[\alpha]_D^{20^\circ} = +238^\circ$  in solution of from 1/2 to 7 per cent. strength. With a later preparation, which was subsequently shown to be non-racemised, the following data were obtained: 4 per cent. solution,  $\alpha_D^{20^\circ}(l=1) = +9.54^\circ$ ;  $d\ 20^\circ/4^\circ = +0.9863$ ;  $[\alpha]_D^{20^\circ} = +242^\circ$ ;  $[M]_D^{20^\circ} = +793^\circ$ .

A preparation made from methyl tartrate and *p*-toluidine and purified as before gave the following result: 3.885 per cent. solution,  $\alpha_D^{20^\circ}(l=1) = +9.23^\circ$ ;  $d\ 20^\circ/4^\circ = +0.986$ ;  $[\alpha]_D^{20^\circ} = +241^\circ$ ;  $[M]_D^{20^\circ} = +790^\circ$ .

As a comparatively high temperature was used in the foregoing preparation from tartaric acid, it was considered necessary to prove more conclusively the absence of racemisation in the product. The specimen

of amide was, therefore, hydrolysed with hydrochloric acid at 120—125° for 5 hours, and the rotation of the resulting tartaric acid measured. The tartaric acid, which was separated in the form of its lead salt, was liberated from this substance by the action of hydrogen sulphide and finally obtained from the filtered solution by evaporation.

A blank experiment was performed by heating some tartaric acid in hydrochloric acid solution in a sealed tube under conditions similar to those employed in the hydrolysis tube.

The following rotations were obtained with 10 per cent. tartaric acid solutions ( $l = 2.962$ ):

|  |         |                                  |         |
|--|---------|----------------------------------|---------|
| Pure tartaric acid (calculated) .....          | + 4°15' | 1st hydrolysis .....             | + 3°59' |
| Pure tartaric acid (used in preparations)..... | + 4°12' | 2nd     " .....                  | + 4° 3' |
|  |         | "     " (blank experiment) ..... | + 4° 2' |

From these results, it is probable that the foregoing specimen of *p*-toluidide was not appreciably racemised, but that a slight racemisation took place during hydrolysis.

A later observation of the rotatory power of this amide gave the following results:

| Temp. | Per cent.<br>solution = $p$ . | $\alpha_D(l=1)$ . | Density. | $[\alpha]_D$ | $[M]_D$ |
|-------|-------------------------------|-------------------|----------|--------------|---------|
| 20°   | 4.502                         | + 10.70°          | 0.987    | + 241°       | + 790   |
| 15    | "                             | 10.87             | 0.994    | 243          | 796     |

### *Tartaric o-Toluidide.*

Tartaric acid (1 mol.) and *o*-toluidine (2 mols.) were heated together for about 8 hours in a flask placed in an oil-bath at 160°. The impure product was boiled with water to get rid of tartaric acid, and the residual di-*o*-toluidide, when crystallised from 70 per cent. alcohol, separated in acicular plates and melted at 184—185°; it was slightly soluble in hot benzene, carbon disulphide, and other common solvents, easily soluble in pyridine, and also in hot alcohol.

0.2694 gave 19.8 c.c. moist nitrogen at 15° and 739.5 mm.  $N = 8.38$ .

$C_{18}H_{20}O_4N_2$  requires  $N = 8.56$  per cent.

### *Rotations in Pyridine.*

This toluidide was also prepared from the methyl ester; it melted at 189°, and when the two specimens were dried the rotations of both



were found to agree, recently distilled pyridine being used as the solvent.

| Temp. | Per cent.<br>solution= $p$ . | $\alpha_D(l=1)$ . | Density. | $[\alpha]_D$ . | $[M]_D$ . |
|-------|------------------------------|-------------------|----------|----------------|-----------|
| 20°   | 3.012                        | + 5.90°           | 0.9845   | + 199°         | + 653°    |
| 20    | 4.994                        | 10.02             | 0.9868   | 203            | 667       |
| 15    | 4.994                        | 10.18             | 0.9936   | 205            | 673       |

*Tartaric m-Toluidide.*

Tartaric acid (1 mol.) and Kahlbaum's purest *m*-toluidine (2 mols.) were heated in a flask placed in an oil-bath at 160° for about 8 hours. The whole became liquid and after a time resolidified owing to the separation of ditoluidide. The product, when purified by the method employed for its *o*- and *p*-isomerides, crystallised from alcohol in needles, and its solubility lay between those of the other two isomerides; it melted at 184°.

0.2309 gave 17.1 c.c. nitrogen at 16.5° and 750 mm.  $N = 8.50$ .

$C_{18}H_{20}O_4N_2$  requires  $N = 8.56$  per cent.

*Rotations in Pyridine.*—The substance is very soluble in pyridine, and in a 2 per cent. solution it gave  $[\alpha]_D = +224.0^\circ$ , and  $224.6^\circ$  after recrystallisation, this constancy indicating the purity of the specimen.

| Per cent.<br>solution= $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d_{20^\circ/4^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------|------------------------------|-------------------------------------|---------------------------|----------------------|
| 15.93                        | + 36.03°                     | 1.012°                              | + 223.6°                  | + 733°               |
| 0.9665                       | 2.13                         | 0.978                               | 225.3                     | 739                  |

*Specimen prepared from the methyl ester (m. p. 184°) gave:*

| Per cent.<br>solution= $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d_{20^\circ/4^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------|------------------------------|-------------------------------------|---------------------------|----------------------|
| 2.009                        | + 4.34°                      | 0.9822                              | + 220°                    | + 722°               |

Specially purified *m*-toluidine from Messrs König (Leipzig) gave specimens of di-*m*-toluidide having the following rotatory power:

*Prepared from Tartaric Acid (m. p. 182—183°).*

| Per cent.<br>solution= $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d_{20^\circ/4^\circ}$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------|------------------------------|-------------------------------------|---------------------------|----------------------|
| 2.121                        | + 4.571°                     | 0.9824                              | + 219°                    | + 720°               |
| 1.705                        | 3.599                        | 0.9822                              | 215                       | 705                  |

*Prepared from Methyl Tartrate (m. p. 182°).*

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[\text{M}]_D^{20}$ . |
|----------------------------|------------------------|------------------------------------|---------------------|-----------------------|
| 2.153                      | + 4.58°                | 0.9329                             | + 217°              | + 710°                |
| 6.65                       | 14.37                  | 0.9934                             | 218                 | 713                   |

Another specimen prepared from Kahlbaum's *m*-toluidine gave the following results :

| Temp. | Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density. | $[\alpha]_D^{20}$ . | $[\text{M}]_D^{20}$ . |
|-------|----------------------------|------------------------|----------|---------------------|-----------------------|
| 20°   | 4.772                      | + 10.64°               | 0.9875   | + 226°              | + 740°                |
| 15    | 4.772                      | 10.80                  | 0.994    | 228                 | 747                   |

*Tartaric  $\alpha$  Naphthylamide,  $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$ .*

$\alpha$ -Naphthylamine (2 mols.) and powdered tartaric acid (1 mol.) were heated in an oil-bath at 170° for 5 hours. The brown product was extracted with boiling dilute hydrochloric acid, and the residue, when crystallised from a mixture of pyridine and alcohol, separated in fine needles, often in large clusters. When washed with alcohol and recrystallised from the above mixture, it melted at 213—214°. The  $\alpha$ -naphthylamide is insoluble in the common solvents except pyridine and hot acetic acid, and dissolves to a less extent in alcohol.

0.1531 gave 9.4 c.c. moist nitrogen at 14° and 739.7 mm.  $\text{N} = 7.03$ .

$\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_2$  requires  $\text{N} = 7.02$  per cent.

*Rotations in Pyridine.*

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density.<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[\text{M}]_D^{20}$ . |
|----------------------------|------------------------|-------------------------------------|---------------------|-----------------------|
| 3.378                      | + 3.28°                | 0.988                               | + 98.3°             | + 393°                |
| 3.806 (recryst.)           | 3.71                   | 0.991                               | 98.4                | 394                   |
| 6.560                      | 6.56                   | 0.997                               | 100.3               | 401                   |
| 1.303                      | 1.25                   | 0.983                               | 97.6                | 390                   |

*Tartaric  $\beta$  Naphthylamide,  $(\text{CHOH})_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$ .*

$\beta$ -Naphthylamine (2 mols.) and tartaric acid (1 mol.) were heated for about 6 hours at 160—170° in an oil-bath. The product was boiled with water and dilute hydrochloric acid, the residue being treated with warm alcohol to extract coloured matter and then crystallised from pyridine. The compound crystallises in plates melting at 279°; it is insoluble in the common solvents, with the exception of alcohol and pyridine; in the former of these, it is slightly soluble, and

dissolves readily in the latter. It differs from the  $\alpha$ -compound in crystalline form, has a much higher rotation and melting point, and is much less soluble.

0.2362 gave 14.2 c.c. moist nitrogen at  $14.2^\circ$  and 742.6 mm.  $N = 6.90$ .

$C_{24}H_{20}O_4N_2$  requires  $N = 7.02$  per cent.

### *Rotations in Pyridine.*

#### *First Specimen.*

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d\ 20^\circ/4^\circ$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------------------------------|------------------------------|------------------------------------|---------------------------|----------------------|
| 1.339                         | + 3.83°                      | 0.984                              | + 291°                    | + 1163°              |
| 2.129                         | 5.96                         | 0.984*                             | 284                       | 1138                 |

\* A different specimen of pyridine.

#### *Second Specimen.*

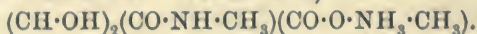
| Per cent.<br>solution = $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d\ 20^\circ/4^\circ$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------------------------------|------------------------------|------------------------------------|---------------------------|----------------------|
| 0.7373                        | + 2.11°                      | 0.9798                             | + 292°                    | + 1169°              |
| 1.185                         | 3.359                        | 0.982                              | 289                       | 1155                 |

The  $\beta$ -naphthylamide was also prepared from methyl tartrate. After purification and recrystallising, the following rotations were obtained:

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br>$d\ 20^\circ/4^\circ$ . | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|-------------------------------|------------------------------|------------------------------------|---------------------------|----------------------|
| 1.316                         | + 3.764°                     | 0.9808                             | + 292°                    | + 1167°              |
| 0.5505                        | 1.566                        | 0.9795                             | 290                       | 1162                 |

### *Tartaric Methylamide, $(CH\cdot OH)_2(CO\cdot NH\cdot CH_3)_2$ .*

An attempt was made to prepare this compound by warming a mixture of methyl tartrate with a 33 per cent. solution of methylamine; the product, after crystallisation from alcohol and benzene, melted at  $187-189^\circ$ , and combustion pointed to its being the methylamine salt of a substituted tartramic acid,



0.1860 gave 23.1 c.c. moist nitrogen at  $11.5^\circ$  and 755 mm.  $N = 14.68$ .

0.2045 „ 25.1 c.c. „ „ „  $9.5^\circ$  „ 754.6 mm.  $N = 14.64$ .

$C_6H_{14}O_5N_2$  requires  $N = 14.43$  per cent.

This substance gives no precipitate with silver nitrate, but, on boiling the solution, silver is precipitated.



The diamide was obtained by distilling the gaseous amine (dried with lime) into a cooled solution of methyl tartrate in anhydrous methylated spirit. After a short time, the amide separated and was recrystallised from alcohol, the melting point being  $189^{\circ}$ ; it gave no precipitate of silver when boiled with silver nitrate solution. The amide is easily soluble in water and pyridine, insoluble in cold alcohol, benzene, ethyl acetate, and carbon disulphide.

0.1980 gave 26.6 c.c. moist nitrogen at  $14^{\circ}$  and 756 mm.  $N = 15.72$ .

$C_6H_{12}O_4N_2$  requires  $N = 15.95$  per cent.

The compound gave a specific rotation in a 3 per cent. pyridine solution of  $+158.0^{\circ}$ , and  $+158.6^{\circ}$  in the same solvent after recrystallisation from alcohol.

#### Rotations in Pyridine.

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^{\circ}$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|----------------------------|------------------------|--------------------------------------|---------------------|----------------|
| 2.988                      | $+4.65^{\circ}$        | 0.985                                | $+158.0^{\circ}$    | $+278^{\circ}$ |
| 2.932 (recryst.)           | 4.60                   | 0.989*                               | 158.6               | 279            |
| 7.679                      | 12.16                  | 1.000                                | 158.3               | 279            |
| 1.433                      | 2.21                   | 0.981                                | 157.2               | 277            |
| 0.684                      | 1.045                  | 0.980                                | 155.9               | 274            |

\* A different specimen of pyridine.

#### Rotations in Water.

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^{\circ}$ . | $[\alpha]_D^{20}$ . | $\alpha_D^{20}$ . |
|----------------------------|------------------------|--------------------------------------|---------------------|-------------------|
| 0.994                      | $+1.44^{\circ}$        | 1.001                                | $+144.7^{\circ}$    | $25.5^{\circ}$    |
| 2.325                      | 3.334                  | 1.005                                | 142.7               | 251               |
| 3.041                      | 4.235                  | 1.006                                | 138.5               | 244               |
| (After boiling)*           | 4.245                  | 1.006                                | 138.8               | 244               |
| 7.475                      | 10.31                  | 1.018                                | 135.5               | 239               |
| 7.774                      | 10.84                  | 1.020                                | 136.7               | 241               |
| 10.35                      | 14.59                  | 1.027                                | 137.3               | 242               |

\* Part of the solution was tared, boiled, cooled, and made up to the original weight; the rotation of this boiled solution was practically identical with that of the original, showing that there is no birotation.

#### Tartaric Ethylamide, $(CH \cdot OH)_2(CO \cdot NH \cdot C_2H_5)_2$ .

A mixture of ethylamine (2 mols.) and methyl tartrate (1 mol.) in anhydrous alcoholic solution slowly deposits the ethylamide on cooling. After distilling off the alcohol, more crystals were obtained, the total yield being 75–80 per cent. The amide, when recrystallised from ethyl acetate and a small quantity of alcohol, was obtained in white,

glistening, felted needles melting at  $210-211^{\circ}$ ; it is easily soluble in water and pyridine, fairly soluble in alcohol, less so in ethyl acetate and benzene, and dissolves in acetic acid.

0.1958 gave 24.1 c.c. moist nitrogen at  $15^{\circ}$  and 735 mm.  $N = 13.93$ .

$C_8H_{10}O_4N_2$  requires  $N = 13.76$  per cent.

The specimen obtained from the first crystallisation had a specific rotation of  $+137.1^{\circ}$  and when recrystallised gave  $+137.9^{\circ}$ . The remaining rotations were determined with the latter specimen.

*Rotations in Pyridine.*

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^{\circ}}(l=1)$ . | Density<br>$d\ 20^{\circ}/4^{\circ}$ . | $[\alpha]_D^{20^{\circ}}$ . | $[M]_D^{20^{\circ}}$ . |
|-------------------------------|--------------------------------|--|-----------------------------|------------------------|
| 3.871                         | $+5.25^{\circ}$                | 0.989                                  | $+137.1^{\circ}$            | $+280^{\circ}$         |
| 3.761                         | 5.125                          | 0.988                                  | 137.9                       | 281                    |
| 5.030                         | 6.83                           | 0.9936                                 | 136.6                       | 279                    |
| 2.401                         | 3.26                           | 0.985                                  | 137.8                       | 281                    |
| 1.049                         | 1.395                          | 0.982                                  | 135.7                       | 277                    |

*Rotations in Water.*

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^{\circ}}(l=1)$ . | Density<br>$d\ 20^{\circ}/4^{\circ}$ . | $[\alpha]_D^{20^{\circ}}$ . | $[M]_D^{20^{\circ}}$ . |
|-------------------------------|--------------------------------|--|-----------------------------|------------------------|
| 1.390                         | $+1.790^{\circ}$               | 1.001                                  | $128.6^{\circ}$             | $+262^{\circ}$         |
| 1.905                         | 2.396                          | 1.002                                  | 125.5                       | 256                    |
| 3.942                         | 4.990                          | 1.007                                  | 125.7                       | 256                    |
| 7.468                         | 9.53                           | 1.017                                  | 125.5                       | 256                    |

*Tartaric Benzylamide,  $(CH \cdot OH)_2(CO \cdot NH \cdot CH_2C_6H_5)_2$ .*

Methyl tartrate (1 mol.) and benzylamine (2 mols.) in alcoholic solution were allowed to react in the cold, when the benzylamide separated in white, glistening plates. On recrystallisation from hot alcohol, it separated either in plates or needles according to the conditions. The amide is easily soluble in pyridine and insoluble in water; it melts at  $199^{\circ}$ .

0.2767 gave 21.1 c.c. moist nitrogen at  $14^{\circ}$  and 731 mm.  $N = 8.63$ .

$C_{13}H_{20}O_4N_2$  requires  $N = 8.56$  per cent.

*Rotations in Pyridine Solution.*

| Per cent.<br>solution = $p$ . | $\alpha_D^{20^{\circ}}(l=1)$ . | Density<br>$d\ 20^{\circ}/4^{\circ}$ . | $[\alpha]_D^{20^{\circ}}$ . | $[M]_D^{20^{\circ}}$ . |
|-------------------------------|--------------------------------|--|-----------------------------|------------------------|
| 5.497                         | $+4.983^{\circ}$               | 0.9911                                 | $+91.5^{\circ}$             | $+300^{\circ}$         |
| 3.461                         | 3.123                          | 0.9861                                 | 91.5                        | 300                    |
| 1.022                         | 0.932                          | 0.9802                                 | (93.0)                      | (305)                  |

*Tartaric Phenylhydrazide*,  $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2$ .

This compound has been prepared by heating methyl tartrate with phenylhydrazine, and was crystallised from alcohol or from glacial acetic acid (Bülow, *Annalen*, 1886, 236, 195; Fischer and Passmore, *Ber.*, 1889, 22, 2734). In alcoholic solution, tartaric acid and phenylhydrazine form diphenylhydrazine tartrate, in distinction to aniline and the toluidines, which form only the mono-salt. The phenylhydrazide can be prepared by heating either the above-mentioned salt or a mixture of phenylhydrazine with an alkyl tartrate or the free acid; when recrystallised from pyridine and water, it melted and decomposed at about  $231^\circ$ .

0.1877 gave 28.2 c.c. moist nitrogen at  $13.7^\circ$  and 744 mm.  $\text{N} = 17.33$ .

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_4$  requires  $\text{N} = 17.02$  per cent.

The specific rotation  $[\alpha]_D^{20}$  of different specimens varied considerably (from  $16^\circ$  to  $24^\circ$ ). These inconsistencies are possibly due to traces of anilide, which would greatly affect the rotatory power. We can only conclude from these figures that the value of  $[\text{M}]_D^{20}$  for the phenylhydrazide is many times smaller than that of the anilide or the toluidide, being probably  $<80^\circ$ . We hope soon to be able to obtain more accurate information as to the rotatory power of this compound, which is being further examined by one of us.

*Tartaric Hydrazide*,  $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ .

This compound was prepared as described by Von Rothenburg (*Ber.*, 1893, 26, 2057). An alcoholic solution of hydrazine hydrate, prepared by the interaction of caustic potash and hydrazine hydrochloride dissolved in alcohol, when treated with methyl tartrate, slowly deposited the hydrazide, which was collected and dried. This compound was insoluble in pyridine, slightly soluble in alcohol, and readily dissolved in water, giving a neutral solution, from which it had a tendency to separate as an oil. The determinations of rotatory power were made on the substance so obtained without recrystallising. Like the amide, it is insoluble in the common solvents except water. It differs from the amide in being much more soluble in water, and the aqueous solution when shaken up with benzaldehyde, forms a benzylidene derivative.



*Rotations in Water.*

| Per cent.<br>solution = <i>p</i> . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br><i>d</i> 20°/4°. | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------------|------------------------------|-----------------------------|---------------------------|----------------------|
| 2.074                              | + 2.206°                     | 1.0058                      | + 97.1°                   | + 173°               |
| 3.264                              | 3.146                        | 1.0105                      | 95.4                      | 170                  |
| 6.552                              | 6.41                         | 1.0257                      | 95.4                      | 170                  |

*Tartaric Benzylidenehydrazide*,  $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_5)_2$ .

This substance, which is described by Von Rothenburg (*loc. cit.*), is obtained on shaking up an aqueous solution of the hydrazide with benzaldehyde; it is slightly soluble in alcohol and more so in pyridine. It was recrystallised from pyridine and gave white, lustrous plates melting at 230° with decomposition.

*Rotations in Pyridine.*

| Per cent.<br>solution = <i>p</i> . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br><i>d</i> 20°/4°. | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------------|------------------------------|-----------------------------|---------------------------|----------------------|
| 0.3826                             | + 0.600°                     | 0.9788                      | + 160.2°                  | + 567°               |
| 0.922                              | 1.411                        | 0.9802                      | 156.1                     | 553                  |
| 1.834                              | 2.826                        | 0.9829                      | 156.8                     | 555                  |

*Tartaric Furfurylidenehydrazide*,  $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_4\text{H}_3\text{O})_2$ .

On shaking up a cold, not too dilute, aqueous solution of the hydrazide of tartaric acid with freshly distilled furfuraldehyde, this compound was precipitated; this was filtered off, thoroughly washed with water, and recrystallised from pyridine and alcohol, when it crystallised in small, irregular plates, melting at about 204°, which tend to become brown.

0.1395 gave 20.4 c.c. moist nitrogen at 15.5° and 746.5 mm.  $N = 16.77$ .

$\text{C}_{14}\text{H}_{14}\text{O}_6\text{N}_4$  requires  $N = 16.82$  per cent.

The rotations in pyridine solution were not very constant, owing, probably, to slight decomposition. After the first crystallisation, the following results were obtained:

| Per cent.<br>solution = <i>p</i> . | $\alpha_D^{20^\circ}(l=1)$ . | Density<br><i>d</i> 20°/4°. | $[\alpha]_D^{20^\circ}$ . | $[M]_D^{20^\circ}$ . |
|------------------------------------|------------------------------|-----------------------------|---------------------------|----------------------|
| 0.8418                             | + 1.82°                      | 0.9802                      | + 220.6°                  | + 737°               |
| 3.054                              | 6.64                         | 0.9890                      | 219.9°                    | 735                  |

*Tartaric Hydrazone of Acetophenone,*  
 $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}_6\text{H}_5)_2$ .

Acetophenone reacts with tartaric hydrazide, forming a hydrazone having similar properties to the above-described aldehydic hydrazones.

The new hydrazone was recrystallised from a mixture of pyridine and alcohol and melted at about  $232^\circ$ .

0.1478 gave 18.9 c.c. of moist nitrogen at  $18.5^\circ$  and 750 mm.  $\text{N} = 14.54$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{N} = 14.7$  per cent.

A 0.747 per cent. solution in pyridine gave the following data:  
 $\alpha_D^{20}(l=1) = +0.760^\circ$ ;  $d_{20}^{20}/4^\circ = 0.9814$ ;  $[\alpha]_D^{20} = +104^\circ$ ;  $[\text{M}]_D^{20} = +397^\circ$ .

*Tartranil*,  $(\text{CH}\cdot\text{OH})_2(\text{CO})_2\cdot\text{NC}_6\text{H}_5$ .—One part of tartaric acid was heated for 4 hours at  $180^\circ$  with 2 parts of aniline in an open flask on the oil-bath. The mass was extracted with boiling water and the solution concentrated until crystallisation took place. The crystals were dissolved in methylated spirit and decolorised with animal charcoal; they somewhat resembled tartranilide in appearance and melted with decomposition at  $225^\circ$ .

The compound is soluble in water, alcohol, and pyridine, but only to a very slight extent in the other common solvents; 100 grams of water and methyl alcohol dissolve 1.3079 and 3.8315 grams of the tartranil respectively at  $20^\circ$ .

0.1994 gave 0.4223  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ .  $\text{C} = 57.76$ ;  $\text{H} = 4.40$ .

0.2004 „ 0.4247  $\text{CO}_2$  „ 0.0791  $\text{H}_2\text{O}$ .  $\text{C} = 57.80$ ;  $\text{H} = 4.39$ .

$\text{C}_{10}\text{H}_9\text{O}_4\text{N}$  requires  $\text{C} = 57.97$  and  $\text{H} = 4.35$  per cent.

*Rotations in (1) Water, (2) Methyl Alcohol, and (3) Pyridine.*

|    | Per cent.<br>solution = p. | $\alpha_D^{20}(l=1)$ . | Density<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[\text{M}]_D^{20}$ . |
|----|----------------------------|------------------------|------------------------------------|---------------------|-----------------------|
| 1. | 0.5964                     | $+0.68^\circ$          | 1.0003                             | $+114^\circ$        | $+236^\circ$          |
|    | 1.2346                     | 1.29                   | 1.0021                             | 104                 | 216                   |
| 2. | 1.3049                     | 1.36                   | 0.7980                             | 131                 | 270                   |
|    | 1.6393                     | 1.70                   | 0.8001                             | 130                 | 268                   |
|    | 3.2258                     | 3.31                   | 0.8077                             | 127                 | 263                   |
| 3. | 0.693                      | 0.89                   | 0.9827                             | 131                 | 271                   |
|    | 4.760                      | 6.23                   | 0.9950                             | 132                 | 272                   |

*Tartaric p-Toluid*,  $(\text{CH}\cdot\text{OH})_2(\text{CO})_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ .

The toluidine hydrogen salt was made by warming together *p*-toluidine (1 mol.) and tartaric acid (1 mol.) until they melt and resolidify, this salt being then heated for about 7 hours in an oil-bath at  $200^\circ$ . The toluid was extracted from the slightly charred mass with boiling water, and, after repeated crystallisation from water, melted at  $235^\circ$  with decomposition; it was soluble in alcohol and pyridine, insoluble in chloroform, benzene, and most of the other organic solvents.

0.2205 gave 12.6 c.c. of moist nitrogen at  $14^\circ$  and 737 mm.  $\text{N} = 6.52$ .

0.2254 gave 0.4943  $\text{CO}_2$  and 0.1008  $\text{H}_2\text{O}$ .  $\text{C} = 59.81$ ;  $\text{H} = 4.97$ .

$\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$  requires  $\text{C} = 59.73$ ;  $\text{H} = 4.98$ ;  $\text{N} = 6.35$  per cent.

*Rotations in (1) Methyl Alcohol, (2) Pyridine.*

|    | Per cent.<br>solution = <i>p</i> . | $\alpha_D^{20}(l=1)$ . | Density<br>$[d]_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}$ . | $[M]_D^{20}$ . |
|----|------------------------------------|------------------------|--------------------------------------|---------------------|----------------|
| 1. | 1.976                              | +1.87°                 | 0.7996                               | +118.3°             | +261°          |
|    | 1.177                              | 1.187                  | 0.7963                               | 126.7               | 280            |
|    | 1.064                              | 1.091                  | 0.7962                               | 128.7               | 284            |
| 2. | 6.317                              | 10.43                  | 0.9971                               | 165.6               | 366            |
|    | 1.93                               | 3.136                  | 0.9838                               | 165.2               | 365            |
|    | 1.36                               | 2.180                  | 0.9818                               | 163.3               | 361            |

*Acetyltartaric o-Toluidide*,  $(\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3)_2(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$ .

The *o*-toluidide of tartaric acid can be acetylated by acetic anhydride (Bischoff, *Ber.*, 1890, 23, 2050), but more easily by warming with acetyl chloride. When hydrochloric acid was evolved only very slowly, the excess of acetyl chloride was distilled off and the residue extracted with a small quantity of alcohol. The main part of the acetyl compound which remained in the residue was crystallised from glacial acetic acid; it separated in a colloidal form from the solvent and was slightly coloured. On washing with ether, the colour was removed, although on drying the substance it again became slightly yellow. The substance, which dried to a fine powder and melted at  $229^\circ$ , was fairly soluble in hot chloroform, alcohol, glacial acetic acid, but less so in benzene; it was easily soluble in pyridine, but insoluble in water.

0.2595 gave 15.5 c.c. of nitrogen at  $12.5^\circ$  and 750 mm.  $\text{N} = 6.98$ .

$\text{C}_{22}\text{H}_{24}\text{O}_6\text{N}_2$  requires  $\text{N} = 6.81$  per cent.



*Rotations in Pyridine.*

| Per cent.<br>solution = p. | $\alpha_D^{20}(l=1).$ | Density<br>$d_{20}^{20}/4^\circ$ . | $[\alpha]_D^{20}.$ | $[M]_D^{20}.$ |
|----------------------------|-----------------------|------------------------------------|--------------------|---------------|
| 5.237                      | +1.016°               | 0.9891                             | +19.61°            | 80.8          |
| 5.315 (recryst.)           | 1.036                 | 0.9895                             | 19.7               | 81.2          |
| 2.594                      | 0.432                 | 0.9830                             | 16.94              | 69.8          |
| 4.492                      | 0.844                 | 0.9872                             | 19.0               | 78.4          |

*Summary of Rotations.*

| $[M]_D^{20}.$<br>Solvent. |           |        |                    | $[M]_D^{20}.$<br>Solvent. |           |        |                    |
|---------------------------|-----------|--------|--------------------|---------------------------|-----------|--------|--------------------|
| Amide.                    | Pyridine. | Water. | Methyl<br>alcohol. | Amide.                    | Pyridine. | Water. | Methyl<br>alcohol. |
| Tartramide .....          | —         | +158°  | +210°              | Hydrazide.....            | —         | +170°  | —                  |
| Anilide .....             | +739°     | —      | 600                | Benzylidene               |           |        |                    |
| p-Toluidide .....         | 793       | —      | —                  | hydrazide ...             | +554°     | —      | —                  |
| o-Toluidide .....         | 667       | —      | —                  | Furfurylidene             |           |        |                    |
| m-Toluidide .....         | 730       | —      | —                  | hydrazide .....           | 736       | —      | —                  |
| $\alpha$ -Naphthylamide   | 400       | —      | —                  | Hydrazone of              |           |        |                    |
| $\beta$ -Naphthylamide    | 1160      | —      | —                  | acetophenone              | 397       | —      | —                  |
| Methylamide ...           | 278       | 240    | —                  | Tartranil .....           | 272       | 216    | 268°               |
| Ethylamide .....          | 279       | 256    | —                  | Tartaric p-Toluil         | 366       | —      | 280                |
| Benzylamide.....          | 300       | —      | —                  | Diacetyltartaric          |           |        |                    |
| Phenylhydrazide (<80)     | —         | —      | —                  | o-toluidide ...           | 80        | —      | —                  |

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### CXXXI.—*Simplification of Zeisel's Method of Methoxyl and Ethoxyl Determinations.*

By W. H. PERKIN, Ph.D., F.R.S.

HEWITT and Moore have recently given an account of a modification of Zeisel's method for the estimation of methoxyl groups (*Trans.*, 1902, 81, 318), in which they replaced the condenser of the original apparatus by a fractionating column. Being desirous of making some methoxyl determinations and not having a suitable fractionating column, the author employed a distilling flask with a neck about 16 inches long attached to the ordinary bulbs containing water and red phosphorus, and kept warm by immersion in water heated at 50°, as recommended by Zeisel. The current of carbon dioxide was supplied by a narrow tube passing down the neck of the retort to within a short distance of the surface of the liquid. The hydriodic acid employed boiled constantly at

126° under 760 mm. pressure (Roscoe gives 127°, 774 mm., Trans., 1861, 13, 161) and had a sp. gr. of about 1.68. The bulb of the distilling flask was heated in glycerin as usual, and an experiment made with this arrangement gave good results.

On examining the water in the bulbs after this operation, it was found that it contained only a minute amount of hydriodic acid.

A second experiment was therefore made, substituting a small tube containing anhydrous potassium carbonate for the bulbs with water and phosphorus, and in this case also a good result was obtained. A third experiment was then made without either bulbs or potassium carbonate, and this arrangement was found to work equally well.

The substance used in these experiments was methyl glyoxime-peroxidetetramethyldimalonylate (this vol., p. 1219), which gave the following numbers:

0.3320 gave 0.4596 AgI. OMe = 18.2.

0.3423 „ 0.4615 AgI. OMe = 17.8.

0.3390 „ 0.4634 AgI. OMe = 18.0.

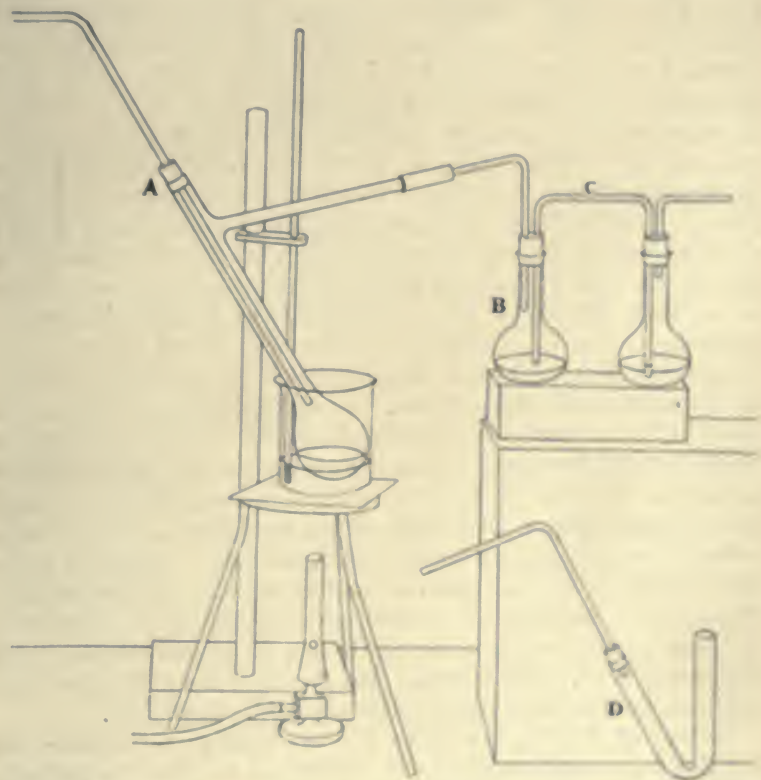
$C_{12}H_{12}O_6N_2(OMe)_2$  requires OMe = 18.1 per cent.

Other substances were then examined by this method, and good results were obtained. It was then thought that perhaps a shorter necked flask might be used, and one with an 8 inch neck was also found to work successfully; a satisfactory result was obtained even with a neck only 5 inches in length, but on the whole an 8 inch neck is perhaps the safest and requires the least attention. It is quite remarkable how the vapour of the hydriodic acid keeps back although a current of carbon dioxide is constantly passing. It is probable that the aqueous acid, although of constant boiling point, gives up a little aqueous vapour which goes forward, and, as it condenses in the neck of the distilling flask, absorbs any hydriodic acid vapour which otherwise might pass, and then runs back into the bulb of the flask.

The actual arrangement ultimately adopted in carrying out the estimation of methoxyl and ethoxyl groups is shown in the accompanying figure and requires but little explanation. It will be seen that one of its great advantages is that the cork *A*, which carries the carbon dioxide tube and closes the neck of the distilling flask, hardly comes into contact with the hydriodic acid, and can be used a great number of times; moreover, tightness may be ensured by the use of a vulcanised india-rubber stopper, whereas in Zeisel's apparatus, and also in that devised by Hewitt and Moore, the cork is constantly exposed to the action of the boiling hydriodic acid and is therefore quickly destroyed.

When using the ordinary arrangement of flasks for the silver solution, the apparatus had to be carefully watched, because if boiling commences in the distilling flask there is a danger of the solution

being drawn back into it, but with the arrangement shown in the figure this cannot happen, because the delivery tube does not enter the silver solution as seen at *B*, so that the iodide formed is absorbed by its surface. The two flasks are connected with a siphon tube, *C*, the end of which in the first flask comes down close to the silver solution, whilst that in the second flask passes into it, so that any methyl iodide vapour carried over with the carbon dioxide from the



first has to bubble through the solution in the second flask, and, in this way, is perfectly absorbed. If any sucking back takes place, a little of the silver solution is drawn through the siphon tube into the first flask, and afterwards forced back again into the second.

In this apparatus, 15 c.c. of the concentrated hydriodic acid (b. p.  $126^{\circ}$ ) are employed, and the substance (0.3—0.35 gram) is weighed in a segment of a very small test-tube, which is then placed in



the neck of the distilling flask and pushed down into the bulb by means of the carbon dioxide tube, the india-rubber stopper carrying the latter being then firmly fixed into the neck. The two flasks, which are charged with the ordinary aqueous-alcoholic solution of silver nitrate, about 20 c.c. in the first and 15 c.c. in the second, are then connected with the distilling flasks by means of vulcanised tubing. The glycerin bath is heated at 130—140°, a constant current of carbon dioxide being passed through the apparatus at the rate of about three or four bubbles in two seconds. In a very short time, the turbidity due to silver iodide and nitrate appears in the silver solution contained in the first flask, the amount formed in the second flask being very small. After a time, the temperature of the glycerin may be raised until it causes the hydriodic acid to boil gently, and the neck of the distilling flask to become heated almost up to the delivery tube, but so that there is no actual distillation into the silver solution. As mentioned by Hewitt and Moore, the operation is often complete in about three-quarters of an hour, but this is not always so, and, as the time varies with different substances, it is best to heat for an hour, the flasks being then disconnected, and a V-tube, *D*, containing a few c.c. of silver solution substituted. The heating is then continued for about 20 minutes, and, if no appreciable quantity of crystalline precipitate forms, the operation may be considered complete, but otherwise the solution should be poured into the bulk in the flasks, a fresh quantity put into the tube, and the process allowed to continue another 20 minutes, and so on until the formation of this precipitate ceases. One compound was heated for about two hours before it ceased to give off methyl iodide, although it dissolved in the hydriodic acid. In some cases, where the substance is attacked with difficulty, the decomposition is greatly facilitated by the addition of acetic anhydride, as proposed by Hewitt and Moore and others. With this arrangement, numbers higher than the calculated were very seldom obtained, showing how well the hydriodic acid is kept back.

Instead of diluting the mixture in the receivers with water and treating it as usually directed, the contents of the flask are gradually added to 50 c.c. of boiling water acidified with nitric acid and contained in a beaker of about 250 c.c. capacity, a small piece of porous porcelain being added to prevent bumping. The boiling is continued until nearly all the alcohol has been driven off and the solution allowed to remain for one hour at the ordinary temperature; the precipitate is then collected on a tared filter and treated in the usual manner. The determinations may be quickly carried out by this method.

Ethoxyl determinations may also be made in this apparatus, but, as found by other experimenters, the numbers are not so accurate as those obtained in the estimation of methoxyl, and are usually some-

what low, a small amount of the ethyl iodide being probably reduced by the hydriodic acid.

The following determinations, made with different classes of substances, will serve to illustrate the trustworthiness of the method.

*Methoxyl Determinations.*

|                               |  | Weight. | Agf.   | CH <sub>3</sub> O<br>found. | CH <sub>3</sub> O<br>calc. |
|-------------------------------|--|---------|--------|-----------------------------|----------------------------|
| The compound                  | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> N <sub>2</sub> (O·CH <sub>3</sub> ) <sup>*</sup> .. | 0·3450  | 0·2850 | 10·9                        | 11·1                       |
| Cryptopine,                   | C <sub>19</sub> H <sub>17</sub> O <sub>3</sub> N(O·CH <sub>3</sub> ) <sub>2</sub> ...              | 0·3480  | 0·4380 | 16·6                        | 16·8                       |
| "                             | C <sub>19</sub> H <sub>17</sub> O <sub>3</sub> N(O·CH <sub>3</sub> ) <sub>2</sub> ...              | 0·3240  | 0·4125 | 16·8†                       | 16·8                       |
| Gnoscopine,                   | C <sub>19</sub> H <sub>11</sub> O <sub>4</sub> N(O·CH <sub>3</sub> ) <sub>3</sub> ...              | 0·3058  | 0·5100 | 22·0                        | 22·5                       |
| "                             | C <sub>19</sub> H <sub>14</sub> O <sub>4</sub> N(O·CH <sub>3</sub> ) <sub>3</sub> ...              | 0·3228  | 0·5366 | 21·9                        | 22·5                       |
| Anisic acid,                  | C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> (O·CH <sub>3</sub> ) .....                            | 0·3039  | 0·4651 | 20·2                        | 20·4                       |
| "                             | C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> (O·CH <sub>3</sub> ) .....                            | 0·3572  | 0·5506 | 20·3                        | 20·4                       |
| Vanillin,                     | C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> (O·CH <sub>3</sub> ) .....                            | 0·3288  | 0·5089 | 20·4                        | 20·4                       |
| $\beta$ -Ethoxynaphthalene,   | C <sub>10</sub> H <sub>7</sub> (OC <sub>2</sub> H <sub>5</sub> )                                   | 0·3278  | 0·4290 | 25·1†                       | 26·1                       |
| "                             | C <sub>10</sub> H <sub>7</sub> (OC <sub>2</sub> H <sub>5</sub> )                                   | 0·3187  | 0·4149 | 24·9†                       | 26·1                       |
| <i>p</i> -Ethoxybenzoic acid, | C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> )                     | 0·4014  | 0·5548 | 26·5                        | 27·1                       |

<sup>\*</sup> This vol., 1229.

In the operations marked † a mixture of 13 c.c. of hydriodic acid and 6·5 c.c. of acetic anhydride was used.

Substances which are volatile in steam sometimes give low numbers owing to oily globules sticking to the glass and not being washed down by the condensed water or acid; this is obviated to some extent if the mixture of hydriodic acid and acetic anhydride is employed, as the acetic acid present dissolves the volatilised substance and carries it back into the hydriodic acid.

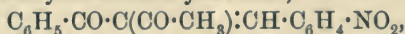
## CXXXII.—The Action of Benzamidine on Olefinic $\beta$ -Diketones.

By SIEGFRIED RUHEMANN.

THE olefinic  $\beta$ -diketones are formed from the aldehydes and  $\beta$ -diketones by the action of either hydrogen chloride or organic bases. The use of hydrogen chloride as a condensing agent will be found more convenient for the preparation of certain members of this group, just as it is for the formation of olefinic  $\beta$ -ketonic esters (this vol., p. 717); especially in those cases where the condensation is not accompanie



the union of the olefinic compound with hydrogen chloride. I have previously shown (*loc. cit.*) that such a union does not take place if, instead of benzaldehyde, *m*-nitrobenzaldehyde reacts with the  $\beta$ -ketonic ester in the presence of hydrogen chloride. Similarly, differences are observed in the behaviour of this condensing agent towards a mixture of aldehydes and  $\beta$ -diketones. Whilst benzaldehyde interacts with acetylacetone, forming benzylideneacetylacetone hydrochloride,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}\cdot\text{CH}_3)\cdot\text{CHCl}\cdot\text{C}_6\text{H}_5$  (Knoevenagel and Werner, *Annalen*, 1894, 281, 79), *m*-nitrobenzaldehyde and the diketone yield *m*-nitrobenzylideneacetylacetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{CO}\cdot\text{CH}_3):\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . In a similar manner, hydrogen chloride acts on a benzene solution of *m*-nitrobenzaldehyde and benzoylacetone, although in this case the yield of *m*-nitrobenzylidenebenzoylacetone,



is very small on account of the ease with which benzoylacetone is decomposed by acids. By using alcohol as a solvent for the aldehyde and the diketone, instead of benzene, and saturating the solution with hydrogen chloride, I have been able to isolate from the product of the reaction, *m*-nitrobenzylideneacetophenone,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , which is formed owing to the elimination of the acetyl group from the diketone.

Whilst the mixture of  $\beta$ -diketones and *m*-nitrobenzaldehyde, on treatment with hydrogen chloride, forms olefinic diketones, the reaction of the aldehyde with the mono-ketone, deoxybenzoin, is analogous to that of benzaldehyde (Klages and Knoevenagel, *Ber.*, 1893, 26, 449), and furnishes *m*-nitrobenzylidenedeoxybenzoin hydrochloride,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}\cdot\text{C}_6\text{H}_5)\cdot\text{CHCl}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ .

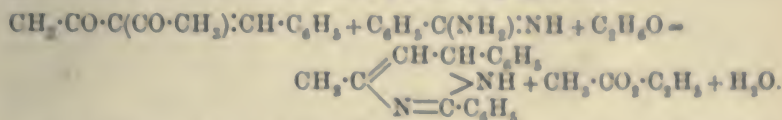
The condensation between *m*-nitrobenzaldehyde and  $\beta$ -diketones may also be effected by piperidine, but different compounds are formed according as the base acts on the dry mixture or on its alcoholic solution. In the first case, the olefinic  $\beta$ -diketone is produced; for instance, *m*-nitrobenzylideneacetylacetone from acetylacetone and *m*-nitrobenzaldehyde, whilst on using alcohol as a solvent, a saturated tetraketone is formed, such as *m*-nitrobenzylidenebisbenzoylacetone,  $[\text{CH}(\text{CO}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{CH}_3]_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , from *m*-nitrobenzaldehyde and benzoylacetone. The same influence of the solvent had been noticed in the course of the experiments on the condensation between *m*-nitrobenzaldehyde and  $\beta$ -ketonic esters (Ruhemann, *loc. cit.*)\*

It has been shown lately (this vol., pp. 374, 717) that benzamidine

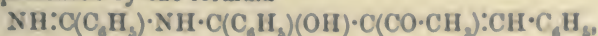
\* I have stated, on p. 717, that ethyl benzylidenebisbenzoylacetate melts at 115–116°, and that after solidification, the melting point is raised to 129–130°. I now find that the ester melts at 131° without previous fusion, if the mixture of the reagents, dissolved in alcohol, is left for 1 to 2 weeks, and the solid, which has separated, is crystallised from alcohol.



condenses with olefinic  $\beta$ -ketonic esters to furnish derivatives of dihydropyrimidone. I have now studied the behaviour of the amidine towards olefinic  $\beta$ -diketones with the view of preparing dihydropyrimidines in accordance with the following equation:

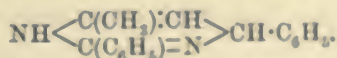


An additive product of the diketone with the amidine is formed at first if the reaction proceeds at the ordinary temperature; the compound, obtained by using benzylidenebenzoylacetone, is, most probably to be represented by the formula



because this structure furnishes a ready explanation of the formation of dibenzamide,  $(\text{C}_6\text{H}_5 \cdot \text{CO})_2\text{NH}$ , which takes place when the substance is heated with hydrochloric acid.

The other olefinic  $\beta$ -diketones undoubtedly form similar additive compounds, but these are transformed if the reaction takes place at  $100^\circ$ . Thus, on boiling the alcoholic solution of the mixture of benzylideneacetylacetone and benzamidine, the additive product loses water and its acetyl group in the form of ethyl acetate, to produce a substance which does not seem to be an open chain compound, since it is not broken up by hydrochloric acid, as is the additive product of benzylidenebenzoylacetone and benzamidine. I am, therefore, inclined to regard it as diphenylmethyldihydropyrimidine,



The behaviour of *m*-nitrobenzylideneacetylacetone towards benzamidine is of special interest, because the additive compound, which may be supposed to be first found, loses its acetyl group and yields *m*-nitrodiphenylmethyldihydropyrimidine,



and not its dihydro-derivative, the hydrogen being probably used up in transforming a part of the product into a hydrogenised compound.

## EXPERIMENTAL.

### *Action of Benzamidine on Benzylideneacetylacetone.*

This reaction takes place when benzylideneacetylacetone, benzamidine hydrochloride, and sodium ethoxide in molecular proportions are dissolved in alcohol and the solution boiled for one hour. On

distillation from the water-bath, ethyl acetate and alcohol are removed, and the viscid residue, which becomes solid when freed from the adhering oil by washing with dilute alcohol, is crystallised from alcohol; it separates in colourless plates melting at 149—150°.

0.1772 gave 0.5330 CO<sub>2</sub> and 0.1060 H<sub>2</sub>O. C = 82.03; H = 6.64.

0.2007 „ 0.6045 CO<sub>2</sub> „ 0.1205 H<sub>2</sub>O. C = 82.15; H = 6.66.

0.2445 „ 24 c.c. moist nitrogen at 21° and 761 mm. N = 11.32.

C<sub>17</sub>H<sub>16</sub>N<sub>2</sub> requires C = 82.25; H = 6.45; N = 11.29 per cent.

This compound, which dissolves with difficulty in cold alcohol and more readily on warming, is freely soluble in glacial acetic acid. It has basic properties and dissolves in hydrochloric acid with the greatest ease, the solution giving a yellow platinichloride which melts under water.

0.2610 gave 0.0553 Pt. Pt = 21.18.

(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>)<sub>2</sub>.H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 21.47 per cent.

In the introduction to this paper, I have expressed the view that the compound C<sub>17</sub>H<sub>16</sub>N<sub>2</sub> is, most probably, diphenylmethyldihydropyrimidine. With the object of oxidising it to the corresponding derivative of pyrimidine, I have saturated its alcoholic solution with nitrogen peroxide, but I find that the transformation does not take place; almost the whole of the original substance is precipitated by caustic potash as a red oil, which gradually solidifies.

#### *m*-Nitrobenzylideneacetylacetone.

*m*-Nitrobenzaldehyde (7.5 grams) gradually dissolves in acetylacetone (5 grams) at the ordinary temperature; on adding 4 drops of piperidine, the solution becomes turbid after a short time and solidifies in the course of a day. The solid is only slightly soluble in cold alcohol, but readily dissolves in hot alcohol, and the solution, on cooling, deposits colourless prisms which melt at 101—102°.

0.2150 gave 0.4860 CO<sub>2</sub> and 0.0955 H<sub>2</sub>O. C = 61.64; H = 4.93.

0.2170 „ 11.8 c.c. moist nitrogen at 22° and 758 mm. N = 6.11.

C<sub>12</sub>H<sub>11</sub>O<sub>4</sub>N requires C = 61.80; H = 4.72; N = 6.0 per cent.

The yield of *m*-nitrobenzylideneacetylacetone is 85—90 per cent. This compound is also formed if the mixture of *m*-nitrobenzaldehyde and acetylacetone is dissolved in as little benzene as possible, and the solution saturated at 0° with dry hydrogen chloride. When left for 2—3 days, the whole sets to a mass of crystals, which, after recrystallisation from alcohol, melt at the same temperature as the foregoing preparation.

*Action of Benzamidine on m-Nitrobenzylideneacetylacetone.*

This reaction takes place on mixing molecular proportions of sodium ethoxide and the hydrochloride of the amidine, dissolved in absolute alcohol, then adding the olefinic diketone (1 mol.) and digesting the mixture for about an hour. On distillation from the water-bath, ethyl acetate and alcohol pass over; the yellow, resinous residue is agitated with dilute hydrochloric acid, when a portion is transformed into a white solid, whilst the other part dissolves. I have tried in vain to purify the solid by crystallisation, but the analyses which have been made with various specimens melting between  $93^{\circ}$  and  $98^{\circ}$ , although differing somewhat from each other, point to the formula  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  for *m*-nitrobenzylideneacetone. The formation of this substance is effected by the elimination of one acetyl group from the olefinic diketone. The acid filtrate from this compound, when treated with an excess of caustic potash, yields a viscid product which gradually hardens. It is washed with water and dissolved in alcohol, when the solution slowly deposits a white substance which readily dissolves in hot alcohol and crystallises from the solution in colourless needles melting at  $137$ — $138^{\circ}$ .

0.2080 gave 0.5340  $\text{CO}_2$  and 0.0850  $\text{H}_2\text{O}$ . C = 70.01; H = 4.54.  
 0.2055 „ 0.5270  $\text{CO}_2$  „ 0.0840  $\text{H}_2\text{O}$ . C = 69.94; H = 4.54.  
 0.2133 „ 26.8 c.c. moist nitrogen at  $22^{\circ}$  and 762 mm. N = 14.26.  
 0.2000 „ 26 c.c. „ „  $22^{\circ}$  „ 750 mm. N = 14.53.  
 $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_2$  requires C = 70.10; H = 4.46; N = 14.43 per cent.

This compound, as stated above, is to be regarded as *m*-nitrodiphenylmethylpyrimidine. It is insoluble in cold hydrochloric acid, and this circumstance, together with the fact that it results from the acid solution of the product of the reaction between benzamidine and the olefinic diketone, leads to the conclusion that it is formed by the gradual change of a substance which is first produced, and which is probably an open chain compound. The pyrimidine derivative, although insoluble in cold hydrochloric acid, dissolves on boiling for some time, and yields a hydrochloride, which crystallises from the acid solution in colourless plates; the salt, however, is unstable, and, on drying at  $100^{\circ}$ , loses hydrogen chloride. It dissolves also in cold concentrated sulphuric acid, and is precipitated unaltered by adding water to the solution.

*m*-Aminodiphenylmethylpyrimidine is obtained by reducing the foregoing compound with iron and hydrochloric acid, adding an excess of caustic potash to the solution, and extracting the precipitate with alcohol. The alcoholic filtrate, on concentration and dilution with



water, yields a white emulsion from which colourless needles gradually separate.

0.1738 gave 23.8 c.c. moist nitrogen at 19° and 772 mm.  $N = 16.0$ .

$C_{17}H_{15}N_3$  requires  $N = 16.09$  per cent.

This compound, which melts at 104—105°, is readily soluble in alcohol or hydrochloric acid, and the acid solution gives, with platinic chloride, an insoluble platinichloride.

*Action of Benzamidine on Benzylidenbenzoylacetone.*

The mixture of benzamidine hydrochloride and sodium ethoxide, dissolved in absolute alcohol, turns yellow on treatment with benzylidenbenzoylacetone. After leaving the product for a day at the ordinary temperature, water is added, when a semi-solid product separates, which slowly becomes hard, and this readily dissolves in alcohol or benzene, the concentrated solutions depositing colourless needles which melt at 132°.

0.2142 gave 0.6083  $CO_2$  and 0.1173  $H_2O$ .  $C = 77.45$ ;  $H = 6.08$ .

0.3020 „ 20 c.c. moist nitrogen at 16° and 747 mm.  $N = 7.57$

$C_{24}H_{22}O_2N_2$  requires  $C = 77.57$ ;  $H = 5.94$ ;  $N = 7.57$  per cent.

This compound is the additive product of benzamidine with benzylidenbenzoylacetone; it dissolves in cold dilute hydrochloric acid, and, on boiling the solution, an oil separates which quickly solidifies. The solid, which crystallises from alcohol in colourless needles melting at 148—149°, is identified as dibenzamido.

0.18579 gave 0.5065  $CO_2$  and 0.0838  $H_2O$ .  $C = 74.38$ ;  $H = 5.01$ .

0.2068 „ 11.4 c.c. moist nitrogen at 190° and 753 mm.  $N = 6.27$ .

$C_{14}H_{11}O_2N$  requires  $C = 74.66$ ;  $H = 4.88$ ;  $N = 6.22$  per cent.

*Action of m-Nitrobenzaldehyde on Benzoylacetone.*

m-Nitrobenzylidenbisbenzoylacetone is formed when the mixture of m-nitrobenzaldehyde (7.5 grams) and benzoylacetone (8 grams), dissolved in as little alcohol as possible, is cooled down by ice, and piperidine (5—6 drops) added to the solution. After 2 days, the whole sets to a mass of crystals, which are washed with alcohol and recrystallised from hot glacial acetic acid, in which they dissolve with great difficulty. The substance gradually separates from this solution in colourless needles which melt and decompose at 229—230°.

0.1815 gave 0.4720  $CO_2$  and 0.0845  $H_2O$ .  $C = 70.92$ ;  $H = 5.17$ .

0.2162 „ 6 c.c. moist nitrogen at 22° and 757 mm.  $N = 3.16$ .

$C_{27}H_{23}O_6N$  requires  $C = 70.90$ ;  $H = 5.03$ ;  $N = 3.06$  per cent.

*m*-Nitrobenzylidenebenzoylacetone is formed by dissolving the mixture of benzoylacetone and *m*-nitrobenzaldehyde in benzene, saturating the ice-cold solution with dry hydrogen chloride, and allowing the solution to remain for about 2 weeks at the ordinary temperature until the benzene has evaporated. The yellow residue is then boiled with light petroleum, which extracts the olefinic diketone, but does not dissolve the resinous by-product. The filtrate, on cooling, deposits light yellow needles which melt at 111–112°.

0.2197 gave 0.5568 CO<sub>2</sub> and 0.0910 H<sub>2</sub>O. C = 69.12; H = 4.60.

0.3078 „ 12.8 c.c. moist nitrogen at 16° and 758 mm. N = 4.83.

C<sub>17</sub>H<sub>13</sub>O<sub>4</sub>N requires C = 69.15; H = 4.41; N = 4.74 per cent.

The compound dissolves in alcohol or benzene with the greatest ease; its alcoholic solution is not coloured by ferric chloride in the cold, but turns red on warming. Owing to the small yield, I have been unable to study the action of benzamidine on this olefinic diketone.

*m*-Nitrobenzylideneacetophenone.—With the view of improving the yield of *m*-nitrobenzylidenebenzoylacetone, I have repeated the former experiment, using alcohol as the solvent instead of benzene. As the alcoholic solution of the reagents, after saturation with dry hydrogen chloride at 0°, rapidly turns red and decomposes, I have only left it for 5–6 hours, subsequently removing the hydrogen chloride and most of the alcohol by evaporation in *vacuo* at 25°, when a solid separates and the odour of acetophenone is perceptible. The solid is freely soluble in benzene, less so in alcohol, and crystallises from the alcoholic solution in light yellow needles which melt at 145°.

0.2027 gave 0.5268 CO<sub>2</sub> and 0.0845 H<sub>2</sub>O. C = 70.88; H = 4.63.

0.3005 „ 14.6 c.c. moist nitrogen at 20° and 761 mm. N = 5.56

C<sub>15</sub>H<sub>11</sub>O<sub>3</sub>N requires C = 71.14; H = 4.34; N = 5.53 per cent.

The yield of this compound is very small, since the greater part of the *m*-nitrobenzylidenebenzoylacetone, which undoubtedly is first formed, undergoes complete decomposition.

#### *Action of m*-Nitrobenzaldehyde on Deoxybenzoin.

This reaction takes place on dissolving, in molecular proportions, the mixture of the aldehyde and the ketone in absolute alcohol, and saturating the ice-cold solution with dry hydrogen chloride. When left overnight, the whole sets to a semi-solid mass, which dissolves in boiling alcohol and separates again in fine needles melting at 166–167°.

0.2620 gave 0.6623  $\text{CO}_2$  and 0.1078  $\text{H}_2\text{O}$ .  $\text{C} = 68.94$ ;  $\text{H} = 4.57$ .  
 0.3079 „ 10.8 c.c. moist nitrogen at  $21^\circ$  and 750 mm.  $\text{N} = 3.93$ .  
 0.1240 gave 0.1240  $\text{AgCl}$ ;  $\text{Cl} = 9.56$ .  
 $\text{C}_{21}\text{H}_{16}\text{O}_3\text{NCl}$  requires  $\text{C} = 68.94$ ;  $\text{H} = 4.38$ ;  $\text{N} = 3.83$ ;  $\text{Cl} = 9.71$   
 per cent.

This compound, therefore, is *m*-nitrobenzylidenedeoxybenzoin hydrochloride. In conclusion, I may state that benzamidine does not react with benzylidenedeoxybenzoin.

GONVILLE AND CAIUS COLLEGE,  
 CAMBRIDGE.

### CXXXIII.—*Dissociation Constants of Trimethylene-carboxylic Acids.*

By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

IN the course of our work on alkyl succinic acids, we have several times required information as to the effect of ring formation on the dissociation constant of a substituted succinic acid, as, for example, in the succeeding paper, where it was necessary to distinguish between an unsaturated and a trimethylene constitution for the acid  $\text{C}_7\text{H}_{10}\text{O}_4$ , obtained by the action of diethylaniline on bromotrimethylsuccinic anhydride. Finding no data available for our purpose, we undertook a comparison of the conductivities of several trimethylene-carboxylic acids with those of the corresponding unsaturated acid, containing two hydrogen atoms less. We think it desirable to record these observations for the guidance of others who may make use of such data in the elucidation of constitutional points. The acids we examined were the following:

*Trimethylenecarboxylic Acid* (b. p.  $182-184^\circ$ ).

0.2566 gave 0.5247  $\text{CO}_2$  and 0.1639  $\text{H}_2\text{O}$ .  $\text{C} = 55.76$ ;  $\text{H} = 7.10$ .

$\text{C}_4\text{H}_6\text{O}_2$  requires  $\text{C} = 55.71$ ;  $\text{H} = 6.98$  per cent.

0.3098 silver salt gave 0.1738  $\text{Ag}$ .  $\text{Ag} = 56.06$ .

$\text{C}_4\text{H}_6\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.95$  per cent.



*Dissociation Constant at 25°.*

$$\mu_{\infty} = 358$$

| $\nu$ . | $\mu_{\infty}$ | m.     | $K = 100k$ . |
|---------|----------------|--------|--------------|
| 17.9    | 6.21           | 0.0174 | 0.00172      |
| 35.8    | 8.76           | 0.0245 | 0.00172      |
| 71.6    | 12.17          | 0.0341 | 0.00169      |

$$K = 0.00171$$

*Trimethylene-1 : 1-dicarboxylic Acid.*—The specimen, kindly supplied by Professor W. H. Perkin, melted at 140—141°.

$$\mu_{\infty} = 356$$

| $\nu$ . | $\mu_{\infty}$ | m.    | $K = 100k$ . |
|---------|----------------|-------|--------------|
| 34.16   | 197.3          | 0.554 | 2.01         |
| 68.32   | 237.9          | 0.670 | 2.00         |
| 136.64  | 273.7          | 0.770 | 1.90         |

$$K = 2.00$$

*cis-Trimethylene-1 : 2-dicarboxylic Acid.*—Prismatic crystals (m. p. 136—137°).

0.1861 gave 0.3140  $\text{CO}_2$  and 0.0768  $\text{H}_2\text{O}$ . C = 46.01 ; H = 4.59.

$\text{C}_5\text{H}_8\text{O}_4$  requires C = 46.16 ; H = 4.62 per cent.

0.2410 silver salt gave 0.1511 Ag. Ag = 62.68.

$\text{C}_5\text{H}_8\text{O}_4\text{Ag}_2$  requires Ag = 62.79 per cent.

*Dissociation Constant at 25°.*

$$\mu_{\infty} = 356$$

| $\nu$ . | $\mu_{\infty}$ | m.     | $K = 100k$ . |
|---------|----------------|--------|--------------|
| 50.7    | 47.74          | 0.1340 | 0.0409       |
| 101.4   | 65.10          | 0.1830 | 0.0406       |
| 202.8   | 88.23          | 0.2480 | 0.0406       |

$$K = 0.040$$

*trans-Trimethylene-1 : 2-dicarboxylic Acid* (m. p. 171—173°).

0.1428 gave 0.2409  $\text{CO}_2$  and 0.0630  $\text{H}_2\text{O}$ . C = 46.0 ; H = 4.90.

$\text{C}_5\text{H}_8\text{O}_4$  requires C = 46.16 ; H = 4.62 per cent.

0.3129 silver salt gave 0.1971 Ag. Ag = 63.02

$\text{C}_5\text{H}_8\text{O}_4\text{Ag}_2$  requires Ag = 62.68 per cent

- *Dissociation Constant at 25°.*

$$\mu_{\infty} = 356$$

| <i>v.</i> | $\mu_{\infty}$ | <i>m.</i> | <i>K</i> = 100 <i>k.</i> |
|-----------|----------------|-----------|--------------------------|
| 95.02     | 46.85          | 0.1316    | 0.0210                   |
| 190.04    | 63.71          | 0.1790    | 0.0205                   |
| 380.08    | 85.90          | 0.2413    | 0.0202                   |

$$K = 0.0206.$$

If we now compare these values with those for the corresponding open chain saturated acids, from which they may be supposed to be derived, we see that in each case the value for the trimethylene acid is the higher of the two, and, in the case of the three dibasic acids, very much higher than the other.

| Acid.   | <i>K.</i> | Acid.                                 | <i>K.</i> |
|---|-----------|---------------------------------------|-----------|
| Trimethylenecarboxylic,<br>$C_4H_6O_2$ .....                    | 0.00171   | Butyric, $C_4H_8O_2$ .....            | 0.00149   |
| Trimethylene-1:1-di-<br>carboxylic, $C_5H_8O_4$ ...             | 2.00      | Dimethylmalonic,<br>$C_5H_8O_4$ ..... | 0.0760    |
| <i>cis</i> -Trimethylene-1:2-di-<br>carboxylic, $C_5H_8O_4$ ... | 0.040     | Methylsuccinic,<br>$C_5H_8O_4$ .....  | 0.00854   |
| <i>trans</i> -Trimethylene-1:2-<br>dicarboxylic, $C_5H_8O_4$    | 0.0205    |                                       |           |

In the succinic series, therefore, it is to be expected that a "trimethylene" formation will be accompanied by a marked increase in the conductivity.

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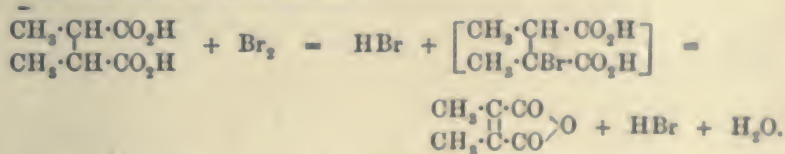
#### CXXXIV.—*The Elimination of Hydrogen Bromide from Bromo-gem-dimethylsuccinic Acid and from Bromo-trimethylsuccinic Anhydride.*

By WILLIAM A. BONE and HERBERT HENSTOCK.

IN continuation of the researches carried out by one of us and Mr. Sprankling on the chemistry of alkyl succinic acids (*Trans.*, 1899, 75, 839; 1900, 77, 654, 1298; 1902, 81, 50), we have recently studied the bromination of these substances and the action of diethylaniline on some of the resultant bromo-acids.

It is unnecessary to make more than a passing reference either to the bromination of succinic acid and its methyl derivative, or to the

important relationships which have been proved to exist between bromosuccinic acid and maleic and fumaric acids on the one hand, and between bromomethylsuccinic acid and citraconic and mesaconic acids on the other. Our knowledge with regard to other alkyl succinic acids is, however, somewhat limited, and in certain respects unsatisfactory. In the case of the two *s*-dimethylsuccinic acids, Hell and Rothberg (*Ber.*, 1889, 22, 66) claim to have obtained bromo-*s*-dimethylsuccinic acid by direct bromination of the acid in the presence of amorphous phosphorus. On the other hand, Bischoff and Voit (*Ber.*, 1890, 23, 645), as well as Auwers and Imhäuser (*Ber.*, 1891, 24, 2233), declare that, in spite of considerable variations in the experimental conditions, they were unable to isolate any product other than the unsaturated pyrocinchonic anhydride,  $C_8H_6O_5$ . Our experiments with *cis*-*s*-dimethylsuccinic acid seem to confirm the observations of the last-named workers, although it is difficult to explain the production of pyrocinchonic anhydride without assuming the intermediate formation of an unstable monobromo-acid in accordance with the following scheme :

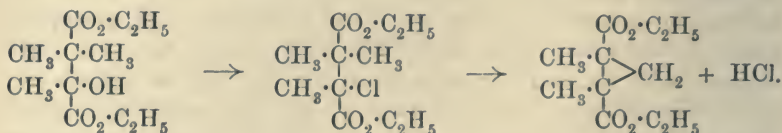


At present, we are making further experiments on this subject.

Some time ago, one of us, with Mr. Sprankling, prepared a bromo-anhydride by the direct action of bromine on trimethylsuccinic acid in sealed tubes at  $130^\circ$ , and also showed that when this substance is heated with diethylaniline it loses hydrogen bromide and yields the anhydride of a new acid,  $C_7H_{10}O_4$  (m. p.  $140-141^\circ$ ). Since this acid decolorised cold alkaline permanganate and readily yielded additive compounds with bromine and also with hydrogen bromide, we described it as the unsaturated methylenedimethylsuccinic acid,  $\begin{array}{c} (\text{CH}_3)_2\text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{H}_2\text{C} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$  (Trans., 1902, 81, 50). Some time previously, however, Vincenzo Paolini (*Gazzetta*, 1900, 30, [ii], 497) had obtained the ethyl ester of an acid,  $C_7H_{10}O_4$ , apparently isomeric with our acid, by the action of phosphorus pentachloride on ethyl hydroxytrimethylsuccinate. His acid melted at  $153-154^\circ$ , and since it neither decolorised cold alkaline permanganate nor exhibited any tendency to form an additive compound with hydrogen bromide at the ordinary temperature, he described it as dimethyltrimethylenedicarboxylic acid. To account for such a result, we must assume the intermediate formation of an unstable ethyl chlorotrimethylsuccinate, which immediately gives rise



to a ring compound by elimination of hydrogen chloride according to the following scheme :

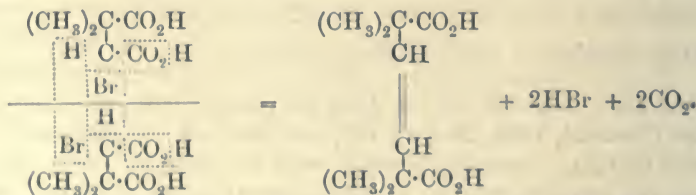


In view of Paolini's interesting observations, we have carefully repeated the former experiments on the action of diethylaniline on bromotrimethylsuccinic anhydride, and have obtained further convincing proof of the unsaturated character of the resulting acid,  $\text{C}_7\text{H}_{10}\text{O}_4$ , by a study of its physical properties. In this connection we are greatly indebted to Dr. W. H. Perkin, sen., who very kindly undertook the determination of the magnetic rotation and refractive power of the ethyl ester of the acid. One of us is now repeating Paolini's work, since it is important that his conclusions should be either confirmed or disproved by independent experiments.

If there is a tendency on the part of halogen substituted succinic acids to give rise to cyclic acids in the manner described above, we might reasonably expect the tendency to be manifested in the case of bromo-*gem*-dimethylsuccinic acid, thus :



We have therefore specially studied this case and find that no such ring formation occurs. On the contrary, when the bromo-acid in question is heated with diethylaniline, a curious bimolecular condensation takes place with simultaneous elimination of hydrogen bromide (2 mols.) and carbon dioxide (2 mols.), according to the following scheme :



The properties of this new *aaa'a'-tetramethyldihydromuconic acid* are fully described in the experimental portion of the paper.

## EXPERIMENTAL.

I. *The Action of Diethylaniline on Bromo-gem-dimethylsuccinic Acid. aaaa'-Tetramethyldihydromuconic Acid.**Bromination of gem-Dimethylsuccinic Acid.*

We find that *gem*-dimethylsuccinic acid is very readily brominated simply by heating it with the calculated quantity of dry bromine in sealed tubes at 140° for 6 or 8 hours. On opening the tubes, a dense stream of hydrogen bromide escapes, the crude bromo-acid swells up considerably, and finally remains in the tube as a light yellow powder. Any slight excess of bromine or hydrogen bromide retained by the substance can be removed by keeping it at 100° for a short time in a current of dry air. The yield is practically quantitative and after recrystallisation from chloroform the pure *bromo-gem-dimethylsuccinic acid* melts at 140°:

0.2110 gave 0.2501 CO<sub>2</sub> and 0.0786 H<sub>2</sub>O. C = 32.3; H = 4.12.

0.2063 „ 0.1697 AgBr. Br = 35.05.

C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>Br requires C = 32.00; H = 4.00; Br = 35.5 per cent.

The acid is very soluble in water, alcohol, ether, and benzene; sparingly so in chloroform, and practically insoluble in light petroleum.

*Action of Diethylaniline on Bromo-gem-dimethylsuccinic Acid.*

Bromo-*gem*-dimethylsuccinic acid (27.5 grams) was digested in 38 grams of redistilled diethylaniline at 130—140° in a reflux apparatus for from 2 to 3 hours. Carbon dioxide was freely evolved, especially during the earlier stages of the experiment. The hot liquid, which darkened in colour, was afterwards poured into a cold solution of 60 grams of caustic potash in 100 c.c. of water and the whole well shaken for some minutes. The diethylaniline was thereupon extracted with ether, leaving a brown solution containing the potassium salt of the new acid. The solution was made strongly acid with 50 per cent. sulphuric acid, and filtered hot from any resinous matter which usually separated at this stage of the experiment. The cold filtrate was repeatedly extracted with washed ether; the ethereal solution, when dried over anhydrous sodium sulphate and distilled to remove the solvent, yielded a slightly brown oil, which rapidly solidified to a mass of crystalline, fan-shaped aggregates. The yield of the crude acid was 85 per cent. of the theoretical.

The amount of carbon dioxide evolved during the digestion with

diethylaniline was determined in a special experiment in which the gas was drawn off from the reaction vessel through (1) a U-tube containing glass beads coated with phosphoric anhydride to arrest any traces of diethylaniline vapour, and (2) a series of absorption tubes containing a clear solution of barium hydroxide. The barium carbonate was afterwards collected, washed, and weighed.

1.351 grams of bromo-*gem*-dimethylsuccinic acid yielded 1.0991 grams of  $\text{BaCO}_3$ , corresponding with 0.2455 gram of  $\text{CO}_2$ .

The equation  $2\text{C}_6\text{H}_9\text{O}_4\text{Br} = \text{C}_{10}\text{H}_{16}\text{O}_4 + 2\text{CO}_2 + 2\text{HBr}$  requires 0.2642 gram of carbon dioxide, the amount actually obtained was therefore 93 per cent. of this quantity.



The crude acid obtained in the foregoing experiment was purified by dissolving it in a slight excess of a strong solution of sodium carbonate; some more resinous matter separated, and this was extracted with chloroform. After acidifying the solution with 50 per cent. sulphuric acid and extracting with ether, we obtained a nearly colourless oil, which soon solidified to a white, crystalline acid melting at  $62^\circ$ .

The acid crystallises well from light petroleum (b. p.  $30-50^\circ$ ), but care should be taken that the solvent does not actually boil during the process of solution, otherwise the acid suddenly creeps up and over the sides of the containing vessel. After some time, nuclei appear on the surface of the cooled solution, and rapidly attract particles from the surrounding liquid. The minute, crystalline aggregates thus formed soon fall to the bottom of the vessel, when they grow into transparent, prismatic crystals some 2 or 3 mm. long. The most perfect crystals we obtained exhibited well-defined prism, pinacoid, and dome facets (either monoclinic or triclinic); most of the crystals melted at  $68^\circ$ , one or two of the purest melting very sharply at  $70^\circ$ .

0.2998 gave 0.6580  $\text{CO}_2$  and 0.2160  $\text{H}_2\text{O}$ . C = 59.84; H = 8.00.

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires C = 60.00; H = 8.00 per cent.

A determination of the molecular weight by the cryoscopic method gave  $M = 190$ ;  $\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $M = 200$ .

The following analysis of the silver salt proves that the acid is dibasic.

0.1320 gave 0.0784 Ag. Ag = 52.27.

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Ag}_2$  requires Ag = 52.10 per cent.

The acid is extremely soluble in water, alcohol, ether, chloroform



and benzene. Its aqueous solution immediately decolorised a cold solution of potassium permanganate rendered alkaline by sodium carbonate.

Its electrical conductivity was determined for four dilutions at 25° with the following results:

$$\mu_{20} = 350.$$

| $c$ . | $\mu_{20}$ | $m$ .  | $100k = K$ . |
|-------|------------|--------|--------------|
| 23    | 6.74       | 0.0192 | 0.001634     |
| 46    | 9.90       | 0.0285 | 0.001817     |
| 92    | 13.86      | 0.0396 | 0.001775     |
| 184   | 19.54      | 0.0558 | 0.001792     |

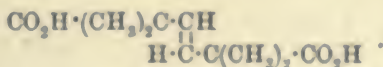
The mean of the last three dilutions is

$$K = 0.001795.$$

This very low value for an unsaturated dibasic acid may be compared with the following:

|              | $K$ . |                  | $K$ .  |
|--------------|-------|------------------|--------|
| Fumaric..... | 0.093 | Mesaconic.....   | 0.0794 |
| Maleic ..... | 1.170 | Citraconic ..... | 0.3400 |

The constant of our new acid is only about one-fifth of that of the *gem*-dimethylsuccinic acid ( $K = 0.00805$ ), which served as the starting point in its preparation. We infer, therefore, that the two carboxyl groups are very widely separated, and that of the two possible stereoisomeric forms of tetramethyldihydromuconic acid, this acid is the fumaroid modification, thus:



This view is also supported by the fact that the acid distilled unchanged under the ordinary pressure; the distillate solidified at once in the receiver, and the solid melted at 68°. Moreover a mixture of equal parts of the solid and the original acid likewise melted at 68°.

When boiled with acetic anhydride, the acid yielded a liquid, resembling an anhydride, which distilled between 116° and 120° under 20 mm. pressure. The liquid did not solidify, even when left for some time in a vacuum over solid potash. It dissolved in boiling water, and, on cooling the solution, a mass of silky needles separated which melted at 60—61°.

Subsequent experiments showed that the acid could be transformed into these needle-like crystals simply by boiling it with dilute sulph-

uric acid. The acid dissolved in the warm liquid and on raising the temperature an oil separated; this redissolved when the liquid was boiled; finally, on cooling, a mass of white needles appeared. These melted at  $61^{\circ}$  and were identical with the needles obtained when the product of the action of acetic anhydride on the original acid was dissolved in boiling water. This curious behaviour suggested the formation of a lactonic acid, or possibly of a dilactone, but subsequent examination of the composition and properties of the acicular crystals did not support this view. Analysis showed that this compound has the same percentage composition as the original acid, thus:

0.1446 gave 0.3162  $\text{CO}_2$  and 0.1074  $\text{H}_2\text{O}$ .  $\text{C} = 59.75$ ;  $\text{H} = 8.20$ .

$\text{C}_{10}\text{H}_{16}\text{O}_7$  requires  $\text{C} = 60.00$ ;  $\text{H} = 8.00$  per cent.

0.1804 silver salt gave 0.0934 Ag.  $\text{Ag} = 51.77$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 52.1$  per cent.

Moreover, its electrical conductivity at  $25^{\circ}$  was almost identical with that of the original acid, thus:

$$\mu_{\infty} = 350.$$

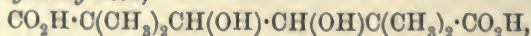
| $v.$ | $\mu_{\infty}$ | $m.$   | $K=100k.$ |
|------|----------------|--------|-----------|
| 40   | 9.32           | 0.0266 | 0.00181   |
| 80   | 13.05          | 0.0373 | 0.00181   |
| 160  | 18.47          | 0.0528 | 0.00184   |
| 320  | 25.90          | 0.0740 | 0.00185   |

$$K = 0.00183.$$

This led us to think that the solid (m. p.  $61^{\circ}$ ) is a dimorphous form of the original acid, a supposition which was strengthened by the fact that on recrystallising the needles from petroleum ether, we obtained prismatic crystals melting at  $68^{\circ}$ , similar to those described on p. 1384.

#### *Oxidation of the Acid with Alkaline Permanganate.*

In order to confirm the formula assigned to our acid, we studied its oxidation with alkaline permanganate at  $0^{\circ}$ . The latter was rapidly decolorised, and we recovered from the liquid a good yield of the corresponding *dihydroxy-acid*,



which melted at  $129-130^{\circ}$ .

0.1050 gave 0.1962  $\text{CO}_2$  and 0.0726  $\text{H}_2\text{O}$ .  $\text{C} = 50.95$ ;  $\text{H} = 7.7$ .

$\text{C}_{10}\text{H}_{18}\text{O}_6$  requires  $\text{C} = 51.2$ ;  $\text{H} = 7.27$  per cent.

## II. The Elimination of Hydrogen Bromide from Bromotrimethylsuccinic Anhydride. Methylene-dimethylsuccinic Acid.

These experiments were undertaken in order to obtain further evidence as to the constitution of the acids obtained by the action of alkalis and diethylaniline on the bromotrimethylsuccinic anhydride described by Bone and Sprankling in a previous paper (*Trans.*, 1902, 81, 50).

### A. Action of Alcoholic Potash. Hydroxytrimethylsuccinic Acid.

To a hot solution of 18 grams of caustic potash in 50 c.c. of methyl alcohol were cautiously added 10 grams of bromotrimethylsuccinic anhydride. The liquid was boiled for 30 minutes, the alcohol distilled off, the residue dissolved in 250 c.c. of water, and the solution evaporated to dryness on a water-bath. Finally, the residue was re-dissolved in water, the solution strongly acidified with dilute sulphuric acid, and extracted with ether. In this way a yellow oil was obtained which, when left overnight, set to a white, crystalline acid. After recrystallisation from hot benzene, the substance melted at 151°. The acid did not decolorise alkaline permanganate, and its properties were identical with those of the hydroxytrimethylsuccinic acid obtained when the product of the condensation of ethyl dimethylacetoacetate and hydrogen cyanide is hydrolysed with sulphuric acid.

0.1640 gave 0.2872 CO<sub>2</sub> and 0.1012 H<sub>2</sub>O. C = 47.70; H = 6.80.

C<sub>7</sub>H<sub>12</sub>O<sub>5</sub> requires C = 47.73. H = 6.82 per cent.

0.1870 silver salt gave 0.1036 Ag. Ag = 55.40.

C<sub>7</sub>H<sub>10</sub>O<sub>5</sub>Ag<sub>2</sub> requires Ag = 55.36 per cent.

The electrical conductivity of the acid was determined at 25°.

$$\mu_{\infty} = 351.$$

| <i>c.</i> | $\mu_{\infty}$ | <i>m.</i> | <i>K</i> = 100 <i>K</i> . |
|-----------|----------------|-----------|---------------------------|
| 14        | 37.51          | 0.1068    | 0.0914                    |
| 28        | 52.31          | 0.1490    | 0.0932                    |
| 56        | 71.77          | 0.2045    | 0.0938                    |
| 112       | 97.10          | 0.2766    | 0.0943                    |

The mean of the last three dilutions: *K* = 0.0938

This value is approximately three times as great as that of the original trimethylsuccinic acid (*K* = 0.0320). Substitution of H by OH in an organic acid almost always increases the conductivity considerably, as the following typical examples show:



|                    | K.     |                        | K.     |
|--------------------|--------|------------------------|--------|
| Succinic acid..... | 0.0067 | Tricarballic acid..... | 0.0224 |
| Malic „ .....      | 0.0395 | Citric „ .....         | 0.1580 |
| Tartaric „ .....   | 0.097  |                        |        |

B. Action of Diethylaniline. Methylene dimethylsuccinic Acid.

The action of diethylaniline on bromotrimethylsuccinic anhydride and the subsequent isolation of the resulting acid,  $C_7H_{10}O_4$ , have already been described by Bone and Sprankling (*loc. cit.*, 1902, 81, 50). We now wish to add that it is very important not to overheat the diethylaniline solution of the bromoanhydride, a temperature of  $120^\circ$  being quite sufficient to effect the elimination of hydrogen bromide. If the temperature rises much beyond  $130^\circ$ , some charring occurs, and the amount and quality of the product are poor. With proper care, the yield of acid,  $C_7H_{10}O_4$ , may be as high as 80 per cent. of the theoretical; the pure acid melts at  $141^\circ$ .

0.2876 gave 0.5624  $CO_2$  and 0.1688  $H_2O$ .  $C = 52.92$ ;  $H = 6.46$ .

$C_7H_{10}O_4$  requires  $C = 53.10$ .  $H = 6.32$  per cent.

0.2575 of the silver salt gave 0.1498 Ag.  $Ag = 58.17$ .

$C_7H_8O_4Ag_2$  requires  $Ag = 58.06$  per cent.

The acid is easily soluble in water, alcohol, and ether; sparingly so in benzene and chloroform, and quite insoluble in light petroleum. It gives an insoluble calcium salt when a solution of the neutral ammonium salt is boiled with calcium chloride.

With acetyl chloride, it yields its own *liquid* anhydride, which distils over between  $210^\circ$  and  $215^\circ$  under atmospheric pressure.

0.2030 gave 0.4480  $CO_2$  and 0.1114  $H_2O$ .  $C = 60.1$ ;  $H = 6.05$ .

$C_7H_8O_3$  requires  $C = 60.0$ ;  $H = 5.71$  per cent.

The acid we obtained by dissolving this anhydride in hot water melted very sharply at  $142.5^\circ$ , and was undoubtedly a very pure specimen.

We shall now discuss the new evidence in favour of the unsaturated formula,  $\begin{array}{c} CH_2 : C \cdot CO_2H \\ | \\ CH_3 > C \cdot CO_2H \\ | \\ CH_3 \end{array}$ , assigned to the acid by Bone and Sprankling in 1902.

(1) In the first place, the purest specimen of the acid obtained rapidly decolorised a cold solution of potassium permanganate made alkaline with pure sodium carbonate. The acid also absorbed bromine or hydrogen bromide in the cold.

(2) The electrical conductivity at 25° was determined with the following results :

$$\mu_{\infty} = 352.$$

| v. | $\mu_{\infty}$ | mm.    | $K = 100L$ |
|----|----------------|--------|------------|
| 10 | 13.76          | 0.0391 | 0.0159     |
| 20 | 19.70          | 0.0560 | 0.0166     |
| 40 | 27.73          | 0.0788 | 0.0168     |
| 80 | 38.50          | 0.1094 | 0.0168     |

Mean of three last dilutions,  $K = 0.0167$ .

This value, which is only half that of the original trimethylsuccinic acid ( $K = 0.0321$ ), is hardly compatible with the supposition of a "trimethylene" constitution for the acid. From the measurements recorded in the preceding paper, we have good reason for believing that the constant of a trimethylenecarboxylic acid would be higher, and in most cases considerably higher, than that of the corresponding open chain saturated acid containing two additional hydrogen atoms. The constant of our new acid is, moreover, about 33 per cent. higher than that of methylenesuccinic (itaconic) acid ( $K = 0.0121$ ), a fact quite in accordance with our earlier observations that alkylation always raises the dissociation constant in the succinic series.

(3) We converted the acid into its diethyl ester by heating it with sulphuric acid and ethyl alcohol in a reflux apparatus. The pure ester was a colourless oil with an ethereal odour; it boiled at 126–127° under 20 mm. pressure.

0.2362 gave 0.5324  $\text{CO}_2$  and 0.1841  $\text{H}_2\text{O}$ .  $\text{C} = 61.47$ ;  $\text{H} = 8.63$ .

$\text{C}_{11}\text{H}_{18}\text{O}_4$  requires  $\text{C} = 61.60$ ;  $\text{H} = 8.41$  per cent.

This oil was sent to Dr. W. H. Perkin, sen., who very kindly determined its refractive power and magnetic rotation. His report, which is very decisive in favour of an "unsaturated" as against a "trimethylene" constitution, is appended.

The determination of the magnetic rotation of the ester,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , gave the following results :

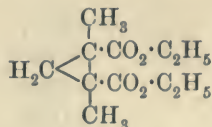
Density:  $d\ 6^\circ/6^\circ = 1.0224$        $d\ 15^\circ/15^\circ = 1.0128$        $d\ 25^\circ/25^\circ = 1.0061$   
 $d\ 10^\circ/10^\circ = 1.0169$        $d\ 20^\circ/20^\circ = 1.0091$

#### Magnetic Rotation.

$t = 16.6^\circ$ .       $\text{Sp. rot.} = 1.0147^\circ$ .       $\text{Mag. rot.} = 11.925$ .

The estimated rotation of ethyl trimethylsuccinate is  $11.205^\circ$ . The value for the ring compound corresponding with this substance and

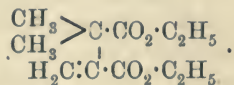
containing two hydrogen atoms less will be  $0.6^\circ$  lower (Trans., 1902, 81, 294), or  $10.605^\circ$ ; and as this is very much lower than the value actually found, therefore, the formula



cannot be correct.

If the rotation of the new compound is compared with that of ethyl trimethylsuccinate, the values are respectively  $11.925$  and  $11.205$ , the difference being  $+0.720$ .

The value found is seen to be considerably higher than that of ethyl trimethylsuccinate, and this is always the case with unsaturated compounds, so that the new ester appears to be an unsaturated substance consistent with the formula :



But this difference of  $+0.720$  is peculiar ; in esters, it is generally as high as  $+1.112$ , unless allyl is present, when it falls to  $+0.918$ , so apparently there must be something in the structure of this compound which causes this unusually small difference. In hydrocarbons, however, the difference for unsaturation is always about  $+0.720^\circ$ , so that this amount does not stand alone in the case of the above compound.

#### *Refractive Power.*

Density  $17.6^\circ/4^\circ = 1.00968$ .

|          | $t = 17.4^\circ$ . | $\mu$ . | $\frac{\mu - 1}{d}$ . | $\frac{\mu - 1}{d} m$ . |
|----------|--------------------|---------|-----------------------|-------------------------|
| $\alpha$ | ,,                 | 1.43577 | 0.43159               | 92.360                  |
| $\beta$  | ,,                 | 1.44535 | 0.44108               | 94.391                  |
| $\gamma$ | ,,                 | 1.45037 | 0.44505               | 95.241                  |

Dispersion,  $\text{H}\gamma - \text{H}\alpha = 2.881$ .

|   |                   | $\text{H}\alpha$ . |
|---|-------------------|--------------------|
| $\text{C}_{11}\text{H}_{18}\text{O}_4$ calculated | Saturated .....   | 90.80              |
|   | Unsaturated ..... | 93.18              |

These numbers correspond with the magnetic rotation, inasmuch as they show that the substance is unsaturated, the difference in this case being, like that of the rotation, somewhat smaller than usual.



In conclusion, the authors desire to express their best thanks to Dr. Perkin, sen., for his kind interest and help in the matter, and to the Research Fund Committee of the Chemical Society for a grant which enabled them to purchase the materials used in the research.

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### CXXXV.—*The Formation of Urea by the Direct Hydrolysis of Lead Cyanate.*

By ALEXANDER CHARLES CUMMING, B.Sc. Kernot Research Scholar in the University of Melbourne.

CRUDE potassium cyanate was dissolved in cold water, the carbonate precipitated by means of barium nitrate, and the solution, after filtering through a cotton wool plug, was treated with lead nitrate. The precipitated lead cyanate, which was washed partly with cold and partly with hot water and dried on the water-bath, was found to consist of aggregates of fine acicular crystals which polarised light.

After three months, a weighed quantity was boiled with a measured excess of standard nitric acid, and when it had all dissolved the remaining acid was estimated by titrating back with standard alkali. One molecule of lead cyanate might be expected to neutralise four equivalents of acid, according to the equation:  $\text{Pb}(\text{CNO})_2 + 4\text{HNO}_3 + 2\text{H}_2\text{O} = \text{Pb}(\text{NO}_3)_2 + 2\text{NH}_4\text{NO}_3 + 2\text{CO}_2$ , but only about one-half this amount was required. It was evident that some change had occurred, and two explanations were possible: (1) that the substance was lead carbonate, formed from the cyanate and water, the ammonium carbonate formed at the same time being lost in the drying,  $\text{Pb}(\text{CNO})_2 + 4\text{H}_2\text{O} = \text{PbCO}_3 + (\text{NH}_4)_2\text{CO}_3$ ; (2) that the precipitate consisted of a mixture of lead carbonate and urea,  $\text{Pb}(\text{CNO})_2 + 2\text{H}_2\text{O} = \text{PbCO}_3 + \text{CON}_2\text{H}_4$ .

The following are the numbers for the first quantitative experiment: 0.280 gram of the supposed lead cyanate neutralised 18.78 c.c. of *N*/10 acid, the calculated amounts for lead cyanate, lead carbonate, and lead carbonate and urea being 38.4, 21.0, and 17.1 c.c. respectively. These figures supported the idea that it was lead carbonate and urea, the amount of the latter being somewhat less than that required by the equation.

Some of the substance was then washed with alcohol, and, on

evaporating off the alcohol, transparent crystals were obtained which gave the qualitative tests for urea.

In order to find out definitely how the action had occurred, a carefully prepared specimen of lead cyanate was boiled with water for one or two minutes, when it was found that almost all the original crystals had disappeared, being replaced by small, amorphous granules and some perfect crystals of lead cyanate, which were very much smaller than the original crystals. The presence of these minute crystals show that lead cyanate must be somewhat soluble in hot water, although it is evidently quickly decomposed by this solvent.

The few original crystals remaining, when examined under a polarising microscope, were found to be granular in structure, and were evidently only pseudomorphs, the granules of lead carbonate having retained the form of the crystalline lead cyanate.

When left for a day in cold water, the lead cyanate crystals were found to contain a few of these granules, which slowly increased in number, but even at the end of two weeks they only represented a small fraction of the whole substance. The hydrolysis of lead cyanate evidently occurs at the ordinary temperature, but exceedingly slowly. All trace of the crystalline structure was destroyed by drying at  $100^{\circ}$ , the change into carbonate being apparently complete.

This method of following the change of lead cyanate into lead carbonate by means of the microscope proved very useful for qualitative work, and gave also a rough estimate of the amount of change.

A portion of the lead cyanate, which had been washed with absolute alcohol immediately after its preparation, retained its crystalline form when dried in a vacuum desiccator.

This loss of the crystalline form is due to the hydrolysis of lead cyanate into amorphous lead carbonate and urea. The latter, being soluble in water and alcohol, may be readily and completely separated from the carbonate by either of these solvents. Some lead cyanate was boiled for several hours with water, the solution filtered, and the precipitate washed with alcohol. The filtrate and washings left, on evaporation, a crystalline mass, which, after one crystallisation from alcohol, was identified as urea by analysis and by the ordinary reactions, including the biuret test and the formation of the sparingly soluble nitrate and oxalate. The crude product, which contained a trace of biuret and a lead salt, melted at  $118^{\circ}$ , but these impurities were completely removed by one crystallisation, after which the melting point was  $129-130^{\circ}$ .

When determined by the freezing point method in aqueous solution, the molecular weight of the specimen was found to be 64.6, the calculated value being 60.1.

Some lead cyanate which had been precipitated and washed with

ice-cold water and drained for a few minutes was washed four times with absolute alcohol and then dried in a vacuum desiccator. As it was found that dry lead cyanate kept perfectly, this sample was used in all the following experiments. To ascertain the yield of urea, 12.327 grams of the dry lead cyanate were heated with water, which was almost at the boiling point, for two hours, and after two days the water was poured off through a filter and the precipitate washed with alcohol. Evaporation of the filtrate and washings gave a crystalline mass, which was dried until of constant weight and then weighed 2.448 grams, being equivalent to 19.8 per cent; the calculated yield of urea from absolutely pure lead cyanate is 20.6 per cent.

The following analytical method, based on the difference in alkalinity of lead cyanate before and after hydrolysis, was used to ascertain to what extent lead cyanate has been hydrolysed in any particular experiment. A weighed quantity of the dry cyanate was treated with a known amount of acid, added either at once or after the salt had been acted on by water in any required manner. After boiling and cooling the mixture, the excess of acid was found by titrating back with alkali.

The specimen of lead cyanate, prepared as already described, was titrated with the following results :

0.1698 neutralised 21.8 c.c. *N*/10 acid.  $\text{Pb}(\text{CNO})_2 = 88.0$ .

0.2000        "        25.9        "        "         $\text{Pb}(\text{CNO})_2 = 89.4$ .

A combustion of the same sample yielded only 1.9 per cent. of moisture. These results lead to the following conclusions : (1) that the lead cyanate is partially hydrolysed in washing, the urea produced being removed during this operation ; (2) that the sample contained 88.7 per cent. of lead cyanate, 9.6 per cent. of lead carbonate, and 6.9 per cent. of moisture.

Portions of this preparation were submitted to further hydrolysis after weighing. In one case, 0.291 gram was twice evaporated to dryness with water on the water-bath, and was then found to neutralise 20.1 c.c. of *N*/10 acid, which indicates that altogether over 98 per cent. of the sample was now hydrolysed into carbonate and urea. This bears out the conclusion, based on the actual yield of urea, that the action is almost quantitative.

In another case, 0.203 gram of the lead cyanate was heated with 20 c.c. of water at 60° for 43 hours. The mixture was then found to neutralise 15.2 c.c. of *N*/10 acid, which indicates a total hydrolysis of almost 90 per cent., so that the action at this temperature is comparatively slow.



*Summary.*

1. Lead cyanate is readily and quantitatively transformed into lead carbonate and urea by direct hydrolysis with boiling water, this reaction furnishing a quick and simple method for obtaining pure urea.

2. The change can be followed qualitatively with a microscope, advantage being taken of the fact that lead cyanate consists of small acicular crystals which polarise light, and that as the action proceeds these become replaced by amorphous granules of lead carbonate.

3. The progress of the action can be followed quantitatively by the alteration in the alkalinity value, which indicates the amount of hydrolysis, since pure lead cyanate neutralises twice as much acid as the products of its hydrolysis.

4. No evidence has been obtained of the formation of ammonium cyanate as an intermediate product. The method is therefore quite different from that of J. Williams (*J. Chem. Soc.*, 1868, 21, 63), who used lead cyanate as an intermediate substance in order to obtain pure ammonium cyanate, from which he prepared urea by Wöhler's well known method.

This work has been carried out in the Chemical Laboratory of the University of Melbourne, and I desire to express my best thanks to Professor Orme Masson for the valuable help he has so kindly given during the progress of this investigation.

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### CXXXVI.—*The Estimation of Hydroxylamine.*

By HUMPHREY OWEN JONES and FREDERICK WILLIAM CARPENTER.

THE authors, while attempting to estimate hydroxylamine in the presence of inorganic salts, found that all the methods hitherto described for the estimation of hydroxylamine were very unreliable in the presence of many substances which would not be expected to interfere with the reaction. Moreover, most of the methods suffered from other defects, such as being affected by the rate of titration and temperature, even when a pure hydroxylamine salt was used.

The authors have therefore worked out another method for the estimation of hydroxylamine, depending on the reduction of cupric oxide to cuprous oxide, which is free from these defects.

Meyerhing (*Ber.*, 1877, 10, 1940), who first investigated methods for

the quantitative estimation of hydroxylamine, proposed to estimate the base in three different ways.

(1) By titration with iodine in presence of magnesia or sodium phosphate. The reaction which takes place was shown to be  $2\text{NH}_2\text{O} + 2\text{I}_2 = \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{HI}$ .

(2) By heating with ferric sulphate and titration of the ferrous salt produced with permanganate or dichromate, the reaction in this case being  $2\text{Fe}_2(\text{SO}_4)_3 + 2\text{NH}_2\text{O} \cdot \text{HCl} = 4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O} + 2\text{HCl}$ .

(3) By titration with standard Fehling's solution. It was proved that nitrous oxide was produced, and the reaction was represented by the equation,  $2\text{NH}_2\text{O} + 4\text{CuO} = \text{N}_2\text{O} + 2\text{Cu}_2\text{O} + 3\text{H}_2\text{O}$ .

Haga (Trans., 1887, 51, 794), who examined the method of titration with iodine, found that the best substance for removing the hydriodic acid was sodium hydrogen carbonate, and that dilution had a marked effect, concentrated solutions requiring less iodine, and very dilute solutions taking more iodine, than that indicated by theory. Moreover, the presence of carbon dioxide or of neutral alkali salts, such as sodium chloride, always increased the quantity of iodine required.

Maxwell Adams (*Amer. Chem. J.*, 1902, 28, 198), who found that the titration with iodine in presence of magnesia and sodium hydrogen carbonate was untrustworthy, accordingly used sodium phosphate, and obtained good results when the proportion of hydroxylamine and the phosphate was kept approximately constant.

The authors find that, on using any of the three reagents proposed to remove hydriodic acid, the results obtained are untrustworthy, and are affected by dilution, by the rate at which iodine solution is added, and, very largely, by the presence of impurities.

The following experiments, selected from a large number, serve to show the magnitude of these effects.

Ten c.c. of a solution of hydroxylamine hydrochloride, which theoretically required 28.6 c.c. of *N*/10 iodine solution, were used for the following experiments.

| Conditions of experiment.                         | c.c. of iodine solution required. |
|---|-----------------------------------|
| Magnesia added .....                              | 25 c.c.                           |
| Sodium phosphate added .....                      | 28.4—28.6 c.c.                    |
| Sodium hydrogen carbonate .....                   | 30.0 c.c.                         |
| Magnesia, 27 c.c. of iodine added rapidly .....   | 29.2 "                            |
| Magnesia + trace of ammonium chloride .....       | 30.6 "                            |
| Magnesia + trace of nickel sulphate .....         | 30.8 "                            |
| Sodium phosphate + trace of nickel sulphate ..... | 29.7—30 c.c.                      |

The end-point in most cases was very slowly attained and uncertain. In estimating pure hydroxylamine solutions, sodium phosphate is undoubtedly the best reagent for removing hydriodic acid, as stated by Maxwell Adams (*loc. cit.*).

This investigator found that Meyeringh's second method was untrustworthy, the amount of permanganate or dichromate required depending on the quantity of ferric salt employed.

The authors found that the amount of ferrous salt produced depended on the strength of the solution of hydroxylamine, the time of heating, and the amounts of ferric salt and acid present, even when the reaction was carried out and the mixture cooled in an atmosphere of carbon dioxide. The quantities of permanganate solution used, in a series of experiments made with the same quantity of hydroxylamine solution under varying conditions, varied between 12.0 c.c. and 15.77 c.c., so that no trustworthy results can be obtained even with pure hydroxylamine solutions.

Simon (*Compt. rend.*, 1902, 135, 1339) proposed to estimate hydroxylamine by titration with potassium permanganate in neutral solution and in presence of rather more than one molecule of normal sodium oxalate to each molecule of hydroxylamine. Under these conditions, the reaction is represented by the equation,  $4(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 = 2\text{MnC}_2\text{O}_4 + 2\text{KHC}_2\text{O}_4 + \text{N}_2\text{O} + 3\text{N}_2 + 15\text{H}_2\text{O}$ .

The authors found several difficulties in carrying out this estimation which rendered it unsuitable for their purpose.

It was found difficult to make solutions of free hydroxylamine and acid solutions of its salts exactly neutral, since the use of an indicator had to be avoided owing to its action in causing the solution to become brown, and thus making it impossible to see the end-point in the subsequent permanganate titration. The amount of permanganate required varied somewhat with the rate of addition and also with the amount of oxalate present. The former effect is not surprising, since the reaction is far from simple, and potassium hydrogen oxalate is one of the final products.

The authors now turned their attention to the reduction of copper oxide by hydroxylamine, as proposed by Meyeringh, but, apparently, never used subsequently, and found that a simple and trustworthy method of estimation could be based on this reaction. The method of titration was found to be inconvenient on account of the uncertainty of the end-point, and, moreover, did not give very consistent results.

It was found that on pouring a solution of pure hydroxylamine hydrochloride into a quantity of boiling Fehling's solution or the copper potassium carbonate solution of Soldaini (*Gazzetta*, 1876, 6,



322) and Ost (*Ber.*, 1890, 23, 1035),\* raising the mixture to the boiling point, collecting the precipitated cuprous oxide on asbestos felt in a Gooch tube crucible of Jena glass, reducing in hydrogen, and weighing the copper thus produced, very constant results were obtained, which, however, did not agree with the theoretical values calculated from the equation  $4\text{CuO} + 2\text{NH}_2\cdot\text{OH} = 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ .

The following are two estimations made by this method, which show the agreement among the results obtained :

(i) 1.6087 grams of  $\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$  in 200 c.c. : 10 c.c. gave 0.1416 gram of Cu or 122.4 grams per gram-molecule of  $\text{NH}_2\cdot\text{OH}$ .

(ii) 1.4812 grams of  $\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$  in 250 c.c. : 10 c.c. gave 0.1046 gram of Cu or 122.7 grams per gram-molecule of  $\text{NH}_2\cdot\text{OH}$ .

The hydroxylamine hydrochloride used throughout these experiments was prepared by crystallising the best commercial specimen obtainable, from hot 98 per cent. alcohol containing a drop of platinic chloride, filtering, and drying in *vacuo* over calcium oxide; it was found to contain  $\text{Cl} = 50.7$  per cent. (theory, 51.0).

The same kind of deviation was observed when the cuprous oxide was estimated by the method proposed by Wood and Berry (*Proc. Camb. Phil. Soc.*, 1902, 12, 2, 97) and by Sonntag (*Chem. Centr.*, 1903, i, 998) for the estimation of sugars. The cuprous oxide, after being collected on asbestos felt in a Gooch's crucible, was washed with boiling water and transferred to a wide-mouthed stoppered bottle, already filled with carbon dioxide. A solution of ferric salt, containing 35 grams of ferric alum and 5 c.c. of strong sulphuric acid in 500 c.c. of water, was added in sufficient quantity to dissolve the cuprous oxide; a portion of the same solution served to completely remove all traces of cuprous oxide from the crucible. On shaking the bottle, the cuprous oxide rapidly dissolved, and the ferrous salt produced was estimated by titration with potassium permanganate:  $4\text{KMnO}_4$  corresponds to  $10\text{NH}_2\cdot\text{OH}$ .

The following experiments correspond with those mentioned above :

Ten c.c. of the first hydroxylamine solution required 21.9 c.c. of permanganate (1 c.c. = 0.00321 gram of  $\text{KMnO}_4$ ) or 60.7 grams of  $\text{KMnO}_4$  per gram-molecule of  $\text{NH}_2\cdot\text{OH}$ .

Ten c.c. of the second solution required 16.1 c.c. of the same solution of permanganate or 60.63 grams of  $\text{KMnO}_4$  per gram-molecule

\* This solution is best made by dissolving 23.5 grams of copper sulphate, 250 grams of potassium carbonate, and 100 grams of potassium hydrogen carbonate in water, warming until complete solution takes place, and making up the volume to one litre.

of  $\text{NH}_2\cdot\text{OH}$ , the value calculated from the copper obtained being 60.71.

The theoretical values of copper and potassium permanganate are 127.2 and 63.2 respectively.

There is, therefore, a deviation of about 5 per cent. from the theoretical value in each case.

Various modifications of the experiment were made in order to find out the cause of this discrepancy. It was found that the relative proportions of the hydroxylamine and copper solution, duration of boiling, and amount of ferric solution used had no effect. Dilution had a slight but decided effect, the amount of permanganate used rose gradually to about 62.0 grams as the solutions were diluted from 1 to 0.05 per cent. of hydroxylamine hydrochloride.

It was then found that practically theoretical results could be obtained if the hydroxylamine solution was added slowly to the copper solution, the latter being well stirred and kept boiling during the addition. About 25 c.c. of the hydroxylamine solution were added from a pipette directly into about 50 c.c. of a well-stirred boiling copper solution. The precipitated oxide was treated in the manner already described, any cuprous oxide deposited on the stirrer being easily dissolved off subsequently by the ferric solution.

The rapid mixture of the hydroxylamine with the copper solution evidently determines the completion of the reaction, and it may be suggested, on the basis of the following experiment, that when hydroxylamine comes into contact with excess of copper oxide the former is oxidised to nitrous oxide according to Meyer's equation,  $4\text{CuO} + 2\text{NH}_3\text{O} = 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ , but that when there is an excess of hydroxylamine, nitrogen is produced, thus:  $2\text{CuO} + 2\text{NH}_2\cdot\text{OH} = \text{Cu}_2\text{O} + \text{N}_2 + 3\text{H}_2\text{O}$ .

This view is supported by the following experiment on the gas evolved from Fehling's solution (the copper potassium carbonate solution is inconvenient on account of the carbon dioxide evolved).

Twenty-five c.c. of a solution containing 0.0948 gram of hydroxylamine hydrochloride gave 16.0 c.c. of gas at  $20^\circ$  and 759 mm. (solution added without stirring). Volume corrected to  $0^\circ$  and 760 mm. = 14.6 c.c. Theory requires 15.2 c.c.

This gas contained nitrous oxide, but on explosion with hydrogen and electrolytic gas, 6.4 c.c. of the gas only gave a contraction of 5.6 c.c., so that it must have contained some nitrogen.

The mixture produced by adding the solution from a dropping funnel to a closed flask was not sufficiently intimate to give pure nitrous oxide.

The following experiments serve to show that, in all cases under

the above-mentioned conditions, the amount of copper obtained and the amount of permanganate used, agree, almost within the limits of experimental error, with the values required by theory.

| Strength of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ solution. | Number of c.c. used. | Weight of Cu obtained. | Grams of Cu per gram-molecule of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ . |
|---|----------------------|------------------------|--|
| 0.7736 grams in 250 c.c.                                      | 25 c.c.              | 0.1414                 | 127.0  |
| " " "   | "                    | 0.1404                 | 126.1  |
| 0.8508 grams in 250 c.c.                                      | "                    | 0.1548                 | 126.6  |

| Strength of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ solution. | Number of c.c. used.   | Number of c.c. of $\text{KMnO}_4$ solution used. | Strength of $\text{KMnO}_4$ solution in grams per c.c. | Number of grams of $\text{KMnO}_4$ per gram-molecule of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ . |
|---|--|--|--|---|
| 1.2057 grams in 250 c.c.                                      | 20 c.c.  | 27.1   | 0.00321  | 62.8  |
| " " "   | "  | 27.0   | "  | 62.5  |
| —   | $\left\{ \begin{array}{l} 20 \text{ c.c.} \\ + 10 \text{ c.c.} \\ \text{H}_2\text{O} \end{array} \right\}$ | 27.2   | "  | 63.0  |
| 0.7736 grams in 250 c.c.                                      | 25 c.c.  | 23.3   | 0.00300  | 62.8  |
| —   | "  | 23.25  | "  | 62.7  |
| —   | "  | 23.45  | "  | 63.2  |
| 0.9484 grams in 250 c.c.                                      | "  | 28.8   | 0.00290  | 63.1  |
| —   | "  | 28.7   | "  | 62.9  |

It is therefore clear that when a solution of a hydroxylamine salt containing not more than 0.5 per cent. of hydroxylamine is introduced into an excess of the boiling alkaline copper solution with stirring, the hydroxylamine is completely oxidised to nitrous oxide, and each molecule produces two molecules of cuprous oxide.

Some of the above determinations were made with Fehling's solution and some with copper potassium carbonate, the results being the same in both cases. The latter solution is much preferable on account of the small change which it undergoes on keeping, and because the cuprous oxide from Fehling's solution must be washed much more thoroughly, otherwise the tartrates interfere with the end-point in the permanganate titration, whereas the substances in the solution when copper potassium carbonate is used do not interfere with the final estimation.

The marked difference in the state of aggregation of the cuprous



oxide precipitated from these two solutions by sugars does not arise when hydroxylamine is used.

The reaction is particularly free from the disturbing effects of impurities, which constitute its chief claim to superiority over other methods. Potassium and sodium salts have no effect. Solutions containing ammonium salts must be boiled sufficiently to expel all the ammonia, in order that no cuprous oxide may be held in solution by the ammonia.

Cobalt, nickel, and zinc salts have no effect when present to the extent of about 0.4 per cent., and although large quantities apparently have no direct influence on the reaction, yet owing to the formation of a precipitate, which greatly delays the filtration, some of the cuprous oxide is probably oxidised, and low results are accordingly obtained. Excess of carbon dioxide or small quantities of alcohol and acetic acid have no effect. Ketoximes have no effect, except on very prolonged boiling, when a very slight reduction is effected.

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## CXXXVII.—*A Study of the Isomerism and Optical Activity of Quinquevalent Nitrogen Compounds.*

By HUMPHREY OWEN JONES, M.A., B.Sc., Fellow of Clare College and Jacksonian Demonstrator in the University of Cambridge.

THE experiments described in this paper were undertaken with the object of investigating more fully the extent and nature of the isomerism among quinquevalent nitrogen compounds, and particularly that isomerism which might theoretically be expected to exist in substituted ammonium salts of the general type  $\text{NR}'\text{R}''\text{R}_3'\text{X}$ . Difficulties were met with both on account of the extremely slow rate at which some of the compounds are formed, and also owing to the fact that it was found impossible to effect some of the desired combinations. It has not been found possible to prepare compounds exhibiting the expected isomerism, but since most of the compounds prepared during the course of the investigation have not hitherto been described,\* and as the non-existence of the isomerism has an important theoretical bearing, the following account of the work is presented to the Society.

The isomerism of quinquevalent nitrogen compounds has already

\* A note was published by the author, in which a few of the compounds first prepared were described (*Proc. Camb. Phil. Soc.*, 1901, 11, 111).

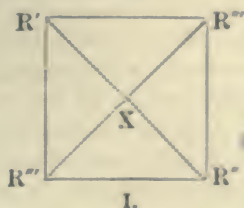
been the subject of a large number of investigations. Le Hel (*Compt. rend.*, 1891, 112, 724) found that *Penicillium glaucum* caused a dilute solution of methylethylpropylisobutylammonium chloride to acquire a small but fugitive rotatory power, and also observed certain differences in crystalline form in some compounds in which three of the radicles were identical. The latter phenomenon must be attributed to dimorphism.

Schryver and Collie (*Chem. News*, 1891, 63, 174) prepared diethyl-isoamylamine platinichloride in the three possible ways, and obtained two compounds differing in crystalline form; this difference, which readily disappeared on recrystallisation, is also probably due to dimorphism.

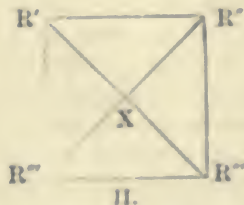
Wedekind (*Ber.*, 1899, 32, 517, 3561) prepared two stable isomerides of phenylbenzylmethylallylammonium iodide, and afterwards described two isomeric methyl benzylallylisobutylammonium-*N*-acetate bromides and two sets of isomeric tetrahydroquinoline derivatives. The existence of the last three pairs of isomerides has since been contradicted by Wedekind himself (*Ber.*, 1902, 35, 3580; 1902, 36, 1158), and hence the first pair stands alone as the only known case of isomerism among quinquevalent nitrogen compounds in which all the five radicles are different. The  $\alpha$ -modification of Wedekind's salt has been resolved into optically active forms by Pope and Peachey (*Trans.*, 1899, 75, 1127), thus conclusively proving the atomic nature of the compound and the stability of its spatial configuration.

Two of the configurations proposed for the nitrogen atom, namely, the "double tetrahedron" structure proposed by Willgerodt and the "pyramid" configuration proposed by Bischoff, explain the above-mentioned results satisfactorily, but the former usually requires the larger number of isomerides and does not explain the phenomena observed by Kipping (see p. 1403), so that the latter will be used throughout the present paper.

It is readily seen that with this configuration two isomerides of the compound  $\text{NR}'\text{R}''\text{R}_3\text{X}$  should exist, which would be represented as follows:

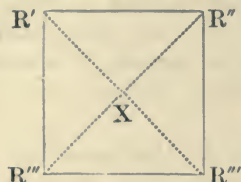


and



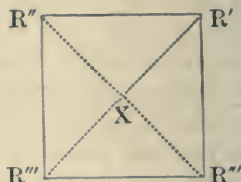
The first of these is planisymmetric and might be expected to exist in one optically inactive form only, the second is asymmetric

and should therefore exist in two enantiomorphous optically active forms, represented thus:



III.

and



IV.

With Willgerodt's configuration, there should be three isomerides and one of these should exist in enantiomorphous forms.

A number of substituted ammonium iodides of this type, produced, with one exception, in two ways, have been examined for optical activity by fractional crystallisation from non-hydroxylic solvents of the *d*-camphorsulphonates (salts of Reychler's acid) and the *d*-bromocamphorsulphonates (Pope and Peachey's method).

In all cases, the compounds produced in different ways were found to be the same, as shown by taking the melting point of a mixture of the two preparations, which themselves had the same melting points, and were also identical in solubility, crystalline appearance, and optical properties. In many cases, when the velocity of reaction between the tertiary amine and the alkyl iodide was sufficiently great, the combination was effected at 0°, and the crystallisation was carried out in an ice-chest at as low a temperature as possible. All the compounds examined were found to be optically inactive; the salts with the above-mentioned optically active acids, on examination in aqueous solution, all showed the molecular rotatory power of salts of the respective acids combined with an inactive base, and the values were not changed by recrystallisation.

In many of the compounds prepared, it is clear that the limit of the so-called "space filling" ("Raum-erfüllung") has nearly been reached, as shown by the extremely small velocity of formation of the compounds. In some cases, the amine and alkyl iodide only combined to a small extent after several months. Also in the case of phenyldibenzylmethylammonium iodide, the compound could not be produced by the union of methyl iodide and dibenzylaniline (Proc., 1901, 17, 205). The absence of isomerism cannot, therefore, be attributed to this cause. Again, unless all the compounds examined are partially racemic, which is very unlikely, the compound formed in all cases is inactive, and therefore has the planisymmetric configuration, which would naturally be the more stable of the two possible configurations. It might be supposed that the absence of activity is due to spontaneous racemisation caused by the greater mobility of the groups used and to the limit of "space



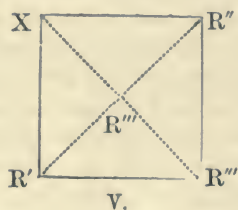
filling " not having been approached to the same extent as in the compound resolved by Pope and Peachey. That this is not so is shown by the fact that two compounds examined by the author, namely, phenylbenzylmethylethylammonium iodide and phenylmethylethylallylammonium iodide, neither of which has been shown to exist in inactive isomerides, can be obtained in optically active forms.

Some explanation of the absence of this isomerism, the existence of which was to be expected from theoretical considerations, must therefore be sought. The author has delayed publication until the results of Kipping's investigations on the isomerism of the compounds of the type  $\text{NRH}_2\text{X}$ , in which R and X both contain an asymmetric carbon atom (Trans., 1900, 77, 861, and 1901, 79, 430, this vol., p. 918, 937), had been brought to a definite conclusion, as it was clear that these experiments had a direct bearing on those described in this paper, and must be considered before any definite theoretical conclusion can be reached.

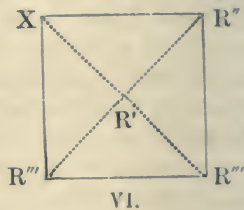
It may fairly be assumed, until direct evidence to the contrary is forthcoming, that the three radicles in a trivalent nitrogen compound lie in one plane, there being as yet no direct evidence either against this assumption or in favour of the suggestion made by Pope and Harvey (Trans., 1901, 79, 838) as applied to the case of nitrogen, that during the change from tri- to quinque-valency a change of valency-direction takes place, and that therefore the three valencies need not be in one plane. This assumption and the Hantzsch-Werner theory of the isomerism of the oximes, &c., are not necessarily incompatible, since it is quite conceivable that the formation of a double union may cause a change in valency-direction giving rise to the isomerides in question, or the isomerism might arise as suggested by Pickering (Trans., 1893, 63, 1072).

The negative result of these experiments was most simply explained by assuming that the three valencies of the trivalent nitrogen atom were in a plane, and that, in becoming quinquevalent, the alkyl haloid,  $\text{RX}$ , was added on symmetrically at right angles to this plane so as to give rise to a molecule having practically the double tetrahedral configuration, rearrangement then took place leading to a change in the valency-direction with the formation of a molecule having the pyramidal configuration. This rearrangement would cause the radicle R to come between two of those already existing in the molecule, and in so doing it would take up a position giving rise to the most symmetrical (and therefore the most stable) configuration, namely, the planisymmetric (I). This hypothesis, however, although it affords a satisfactory explanation of the author's experiments, will not explain the existence of the isomerides observed by Kipping unless it is assumed that in the one case the rearrangement has occurred with the production of one isomeride, whereas in the other it has not taken place at all.

Kipping (this vol., 949) has suggested two hypotheses which explain the formation of two isomeric *d*-hydrindamine *d*-camphorsulphonates; the first assumes that the new radicles, H and X, are added to the trivalent nitrogen, in which the three existing groups are in one plane, in such a way that a pyramidal configuration arises. In this case, it is necessary to make the further assumption that the addition can take place in any one of the three planes of the original triangular configuration, or else this kind of isomerism would not arise, since it vanishes if the asymmetric carbon atom be made to occupy the apex of the pyramid. This hypothesis demands that, in the addition of  $R''X$  to  $NR'R''R'''$ , the compound which arises should correspond with one of the types:



or



both of which should exist in optical antipodes. None of the compounds produced in this way could be resolved into optically active forms: hence this hypothesis does not explain the results of the author's experiments.

The second hypothesis is that, addition having taken place as above, a molecular transformation occurs during which the acidic radicle changes positions with one of the hydrogen atoms of the original amine, thus giving rise to one isomeride, the other being the untransformed additive product. This hypothesis will explain the formation of the planisymmetric compound by the addition of  $R''X$  to  $NR'R''R'''$  and  $R'X$  to  $NR'R_2R'''$ , if, as above, it is assumed that the addition can take place in any one of the three possible planes. It is clear, however, that in this case also, the untransformed product should be an isomeric substance of the existence of which there is no evidence. The slight difference observed by Kipping between the two hydrindamine hydrochlorides derived from the  $\alpha$ - and  $\beta$ -camphorsulphonates, which could only be shown by reconvertng them into the camphorsulphonates (this vol., 943) does not exist in the present instance. The camphorsulphonates prepared from two specimens of phenylbenzylidimethylammonium iodide, produced in one case by the addition of methyl iodide and in the other by the addition of benzyl iodide, are identical in every respect, as are also the camphorsulphonates and the bromocamphorsulphonates obtained from two



specimens of phenyldimethylisobutylammonium iodide prepared in the two possible ways.

The existence of the untransformed product as a stable isomeride is probably due to some special circumstance, as, for instance, the presence of two asymmetric carbon atoms in the case of the hydrindamine camphorsulphonates. In the light of the abnormal behaviour of Kipping's  $\beta$ -isomeride, it was considered advisable to obtain the camphorsulphonate of Wedekind's  $\beta$ -compound and to see if it behaved in a similarly anomalous manner. This was unfortunately not found practicable on account of the extremely small yield of the  $\beta$ -iodide which was obtained.

The question of the existence of optical activity in cyclic ammonium compounds of the pyridine and tetrahydroquinoline series has also been investigated. Theoretically,  $\alpha$ - and  $\beta$ -substituted pyridinium compounds and tetrahydroquinoline derivatives,  $C_6H_{10}NR'R''X$ , should exist as optical antipodes, since the molecules of these compounds have no plane of symmetry. Piperidinium compounds, on the other hand, can take up a planisymmetric configuration, and hence would not be expected to exist in optically active forms.\*

The author has submitted the camphorsulphonates and bromocamphorsulphonates of several of these salts to a long series of crystallisations from non-hydroxylic solvents, but in all cases the molecular rotatory powers of the salts were practically identical with those of salts of the respective acids and inactive bases. It is possible, although not likely, either that all the salts examined are partially racemic or that there is some other hitherto unsuspected reason for the unsuccessful attempts to resolve these compounds. The absence of activity in these compounds is inexplicable on the current views as

\* Since the above was written, Barrowcliff and Kipping (this vol., p. 1141) have published an account of an unsuccessful attempt to resolve three piperidinium compounds. It may therefore be concluded that these compounds are symmetrical.

Wedekind has also recently (*Zeit. physikal. Chem.*, 1903, 45, 235) given an account of his unsuccessful attempts to resolve *p*-tolylbenzylmethylallylammonium iodide into active forms by the fractional crystallisation of the *d*-camphorsulphonate. This salt is very similar in structure to that resolved by Pope and Peachey, and might certainly be expected to undergo resolution in a similar manner, whereas it behaves quite differently. It may therefore be of interest to record a similar unsuccessful attempt to resolve phenylmethylethylallylammonium camphorsulphonate, a salt which crystallised readily in lustrous prisms melting at 145–150°. After several crystallisations, two successive fractions gave  $[M]_D = 49.1^\circ$  and  $50.7^\circ$  respectively; then, after three more crystallisations, the value of  $[M]_D$  was  $51.2^\circ$ , a value very close to that of the acidic ion,  $51.7^\circ$ . The base was, however, apparently resolved by the crystallisation of the *d*-bromocamphorsulphonate. The fact that unexpected difficulties thus arise in the resolution of nitrogen compounds is of considerable interest, and may, as suggested, account for the non-resolution of the cyclic compounds.



to their constitution, and there is no evidence in support of any one of the possible explanations which might be suggested to account for this unexpected phenomenon.

### EXPERIMENTAL.

*Phenyldimethylallylammonium iodide* was prepared by mixing molecular quantities of dimethylaniline and allyl iodide in the cold; the mass, which solidified in about twenty-four hours, was pressed out on a porous plate, and, when crystallised several times from a mixture of absolute alcohol and ether, separated in colourless, prismatic crystals melting at 86—87°. It was found to be identical in every respect with that obtained by the union of methyl iodide with methylallylaniline, even when both combinations were allowed to take place at 0° and recrystallisation carried out at a comparatively low temperature.

- I. 0.143 gave 0.241 CO<sub>2</sub> and 0.074 H<sub>2</sub>O. C = 46.0; H = 5.73.  
 II. 0.3857 on titration required 13.3 c.c. *N*/10 AgNO<sub>3</sub>. I = 43.8.  
 C<sub>11</sub>H<sub>16</sub>NI requires C = 45.83; H = 5.55; I = 43.9 per cent.

*Phenyldimethylallylammonium d-camphorsulphonate* was prepared by mixing together molecular quantities of the iodide (18 grams) and Reychler's silver *d*-camphorsulphonate (20 grams) with ethyl acetate and a few drops of alcohol and heating for about one hour on the water-bath, after filtering and evaporating. The gummy residue, which readily becomes crystalline on rubbing, is very sparingly soluble in ether, but readily soluble in ethyl acetate, chloroform, and fairly so in benzene; it crystallises in monoclinic, colourless plates, which melt sharply at 156°.

- I. 0.3774 gave 12.9 c.c. moist nitrogen at 21° and 756 mm. N = 3.89.  
 II. 0.1668 gave 0.1231 PbSO<sub>4</sub>. S = 7.8.  
 C<sub>21</sub>H<sub>31</sub>O<sub>4</sub>NS requires N = 3.56; S = 8.14 per cent.

The rotatory powers for sodium light of two specimens, repeatedly crystallised respectively from ethyl acetate and from a mixture of benzene and chloroform, were determined in aqueous solution by means of a half shadow polarimeter by Schmidt and Haensch, for the use of which the author is indebted to Mr. F. G. Hopkins.

- 0.779 in 25 c.c. gave  $\alpha_D = 0.81^\circ$  in a 200 mm. tube;  $[\alpha]_D = 13.0^\circ$  and  $[M]_D = 51.1^\circ$ .  
 1.1856 in 35 c.c. gave  $\alpha_D = 1.78^\circ$  in a 400 mm. tube;  $[\alpha]_D = 13.15^\circ$  and  $[M]_D = 51.66^\circ$ .

$[M]_D$  for compounds of the acid with an inactive base is 51.7° according to Pope and Peachey (Trans., 1899, 75, 1086), so that the radicle,  $NPhMe_2 \cdot C_3H_7$ , is inactive.

*Phenyldimethylpropylammonium Iodide.*

(1) Methylpropylaniline, prepared according to Claus and Hirzel's method (*Ber.*, 1886, 19, 2786), was found to boil at 215—217°. A mixture of molecular quantities of the amine and methyl iodide gradually set to a transparent, gummy mass, which was with difficulty induced to crystallise by repeatedly dissolving in alcohol and adding ether until the substance was partially precipitated as an oil, and then allowing the turbid solution to remain until the precipitated oil became crystalline, after which more ether was added. Colourless prisms soluble in acetone, ethyl acetate, and alcohol were obtained which, when recrystallised either from ethyl acetate or from a mixture of alcohol and ether, melted at 68.5°.

(2) Combination of dimethylaniline and propyl iodide took place slowly, a gummy mass being gradually formed which, when dissolved in cold alcohol and treated with ether until a turbidity was produced, crystallised out in large, white crystals melting at 65—66°. After repeated crystallisations the crystals melted at 68.5°, and did not depress the melting point of the preceding preparation.

0.155 gave 0.2572  $CO_2$  and 0.0845  $H_2O$ .  $C = 45.26$ ;  $H = 6.06$ .

$C_{11}H_{18}NI$  requires  $C = 45.36$ ;  $H = 6.17$  per cent.

The corresponding *d*-camphorsulphonate is crystalline.

*Phenylmethyldipropylammonium Iodide.*

(1) Dipropylaniline was prepared by Lippmann and Fleissner's method (*Monatsh.*, 1871, 3, 711); its boiling point was 238° under 750 mm. pressure.

Molecular quantities of the base and methyl iodide were mixed and allowed to remain for about 2 days, when colourless crystals began to separate; these were very soluble in alcohol, somewhat less so in ethyl acetate, very sparingly so in ether and light petroleum. The crude salt melted at 135—137°, but after repeated crystallisation from ethyl acetate and a mixture of alcohol and ether the melting point was 156°.

(2) A mixture of molecular quantities of methylpropylaniline and propyl iodide soon deposited a viscid mass, containing some crystals, and finally set to a crystalline solid which was repeatedly crystallised from alcohol and ether, when leaf-like crystals separated melting at

154—155°. A mixture of this with the foregoing preparation also melted at this temperature.

0.1455 gave 0.2588 CO<sub>2</sub> and 0.0897 H<sub>2</sub>O. C = 48.51; H = 6.85.

C<sub>13</sub>H<sub>22</sub>NI requires C = 48.8; H = 6.86 per cent.

*Phenyldimethylisobutylammonium iodide.*

(1) A mixture of dimethylaniline and isobutyl iodide in molecular quantities very slowly deposited a small quantity of needle-like crystals, which melted at 154—155°, and when crystallised from dilute alcohol melted at 155—156°; by repeated crystallisation, the melting point may be raised a little higher, and in one case it reached 160°. The melting points of this and certain other compounds of this class were found to become slightly lowered by keeping the compound in an ordinary stoppered bottle for a few weeks or longer.

(2) Methylisobutylaniline was found to be very difficult to produce in a state approaching purity. On mixing methylaniline with isobutyl iodide or isobutylaniline with methyl iodide, treating the solid product with caustic potash, separating, drying, and distilling the liquid obtained, the boiling point varied continuously, and after repeated fractionation the greater part finally distilled between 220° and 230°. This liquid rapidly combined with methyl iodide and formed a solid crystalline substance which was found to be phenyltrimethylammonium iodide. Therefore, in each case, the main product was dimethylaniline. This change is of interest, since it shows that the methyl group can behave like the benzyl group in the transformations of benzylaniline and dibenzylamine observed by Wedekind and the author respectively; further, in the case of the action of methyl iodide on isobutylaniline, the reaction is somewhat analogous to the replacement of benzyl by methyl observed in certain ammonium salts (Proc., *loc. cit.*).

By heating together two molecular proportions of methylaniline and one of isobutyl bromide on a water-bath, filtering off the solid methylaniline hydrobromide, and repeatedly fractionating the oil, a liquid was obtained having a constant boiling point of 227—228°. This product, when mixed with a gram-molecule of methyl iodide and left for about a week, yielded an almost solid mass of crystals which were repeatedly crystallised from alcohol and ether, and finally from ethyl acetate. A small quantity of phenyltrimethylammonium iodide was obtained from the first fractions, but the more soluble part was found to reach a constant melting point of 155—156°, which was not changed by the presence of an equal quantity of the substance produced by the first method (1). The two compounds are therefore identical.

0.1820 gave 0.3145 CO<sub>2</sub> and 0.1120 H<sub>2</sub>O. C = 47.12; H = 6.77.

C<sub>12</sub>H<sub>20</sub>NI requires C = 47.21; H = 6.55 per cent.



*Phenylidimethylisobutylammonium d-camphorsulphonate*, prepared in the same way as the other camphorsulphonates, crystallises readily, and is sparingly soluble in ethyl acetate and acetone, but very readily so in methylene diethyl ether. When crystallised repeatedly from a warm mixture of ethyl acetate and methylene ether, it was obtained in colourless needles melting at 190—192°.

After four recrystallisations, its rotatory power was determined in aqueous solution.

0.4325 in 25 c.c. gave  $\alpha_D = 0.41^\circ$  in a 200 mm. tube.  $[\alpha]_D = 11.86^\circ$  and  $[M]_D = 48.6^\circ$ .

The radicle  $NPhMe_3 \cdot C_4H_9$  is therefore inactive.

#### *Phenylbenzylidimethylammonium Iodide.*

(1) Dimethylaniline and benzyl iodide, when mixed in molecular proportion, rapidly set to a solid mass, which, after washing with ether, was crystallised repeatedly from alcohol. The salt then melted sharply at 165°, after becoming brown at 158°.

(2) Benzylmethylaniline was prepared by the action of benzyl chloride on methylaniline, as described by Wedekind. Molecular proportions of the amine and methyl iodide began to deposit solid almost immediately, and after 36 hours, about 30 per cent. had combined. The solid was crystallised several times from absolute alcohol; the melting point after one crystallisation was 157°, rising to 164.5° after four crystallisations. The compound, prepared at 0° and crystallised at the same temperature, also melted at 164—165°. The compound prepared by method (1) was shown to be identical with this by melting a mixture of the two.

0.1262 gave 0.2456  $CO_2$  and 0.0604  $H_2O$ . C = 53.06; H = 5.32.

$C_{15}H_{15}NI$  requires C = 53.09; H = 5.32 per cent.

*Phenylbenzylidimethylammonium d-camphorsulphonate* was prepared both from the iodide and also in larger quantity from phenylbenzylidimethylammonium chloride,  $NPhMe_3(C_7H_7) \cdot Cl, H_2O$  (Michler and Gradmann, *Ber.*, 1877, 10, 2079).

The chloride used was repeatedly crystallised from water and found to contain 14.2 per cent. of chlorine, whereas theory requires 14.3. The chloride or iodide, when boiled with the theoretical quantity of silver *d*-camphorsulphonate and some moist chloroform, filtered, and evaporated to dryness, yielded a product which crystallised readily, and was found to be very sparingly soluble in ethyl acetate, acetone, and light petroleum, although dissolving fairly readily in chloroform. The salt, when crystallised several times from a mixture of chloroform and light petroleum, formed colourless needles which melted at 189°.

0.1223 gave 0.3022  $\text{CO}_2$  and 0.0791  $\text{H}_2\text{O}$ .  $\text{C}=67.38$ ;  $\text{H}=7.2$ .

$\text{C}_{25}\text{H}_{35}\text{O}_4\text{NS}$  requires  $\text{C}=67.71$ ;  $\text{H}=7.4$  per cent.

The rotatory power was determined in aqueous solution in the manner already described.

1.224 in 35 c.c. gave  $\alpha_D=1.63^\circ$  in a 400 mm. tube.  $[\alpha]_D=11.65^\circ$ , and  $[\text{M}]_D=51.62^\circ$ .

This value had not been appreciably altered by repeated crystallisation. The radicle  $\text{NPhMe}_2\cdot\text{C}_7\text{H}_7$  is therefore inactive.

#### *Phenyldibenzylmethyllummonium Iodide.*

Benzyl iodide and benzylmethylaniline combined readily; a mixture of the two substances in molecular proportion rapidly became cold, and in a few hours had set to a pale yellow gum, which subsequently crystallised, about 89 per cent. of the reagents having combined. The product was fairly pure, as shown by the following nitrogen determination:

0.312 gave 10.3 c.c. nitrogen at  $19^\circ$  and 770 mm.  $\text{N}=3.85$ .

$\text{C}_{21}\text{H}_{22}\text{NI}$  requires  $\text{N}=3.38$  per cent.

The salt, when purified by repeated crystallisation from hot absolute alcohol, was obtained in colourless prisms melting at  $134\text{--}135^\circ$ ; it was very soluble in chloroform and very sparingly so in water.

0.1220 gave 0.2710  $\text{CO}_2$  and 0.0610  $\text{H}_2\text{O}$ .  $\text{C}=60.60$ ;  $\text{H}=5.53$ .

$\text{C}_{21}\text{H}_{22}\text{NI}$  requires  $\text{C}=60.7$ ;  $\text{H}=5.30$  per cent.

As the camphorsulphonate was found to crystallise with a molecule of chloroform of crystallisation, it was expected that the iodide would behave similarly. A specimen crystallised from a mixture of chloroform and ether melted slowly at about  $130^\circ$ ; the following analytical result shows that the specimen does not contain chloroform:

0.1264 gave 0.2821  $\text{CO}_2$  and 0.0635  $\text{H}_2\text{O}$ .  $\text{C}=60.8$ ;  $\text{H}=5.58$  per cent.

#### *Phenyldibenzylmethyllummonium Chloride.*

Benzylmethylaniline and benzyl chloride do not combine, even when left for months in the cold or after heating for several hours. The chloride, which was accordingly produced by the action of silver chloride on a warm alcoholic solution of the iodide and purified by crystallisation from alcohol and ether, separated in colourless needles melting at  $159\text{--}161^\circ$ ; it appears to be much more stable than the iodide, since the latter, when heated in alcoholic solution, evolves a strong odour of benzyl iodide, whereas no benzyl chloride can be detected when the former is similarly treated.

The analysis of a specimen, dried in a vacuum, gave the following result :

0.1095 gave 0.3126  $\text{CO}_2$  and 0.0668  $\text{H}_2\text{O}$ .  $\text{C} = 77.8$ ;  $\text{H} = 6.7$ .

$\text{C}_{21}\text{H}_{22}\text{NCl}$  requires  $\text{C} = 78.2$ ;  $\text{H} = 6.80$  per cent.

All attempts to cause dibenzylaniline to combine with methyl iodide were abortive; there was practically no reaction either in the cold after several months or on gently warming. When the mixture was heated at  $100^\circ$  in a sealed tube, benzyl iodide was formed and a crystalline solid was produced which was found to be phenyltrimethylammonium iodide, the two benzyl groups having been removed as benzyl iodide and replaced by methyl groups, whilst the dimethylaniline thus produced combined with a molecule of methyl iodide (Proc., 1901, 17, 205).

*Phenyldibenzylmethylammonium d-camphorsulphonate* was prepared in the same way as the other camphorsulphonates, a mixture of moist ethyl acetate and acetone being used as solvent; the viscid residue solidified when left in a desiccator and stirred at intervals. The salt was found to be very sparingly soluble in dry ethyl acetate and acetone but much more so in these solvents when slightly moist; it dissolved fairly readily in chloroform, alcohol, and methylene diethyl ether. A specimen crystallised repeatedly from chloroform, and then from a mixture of chloroform and benzene, separated in fine needles which had a great tendency to aggregate into sheaves; it melted slowly at  $130$ – $137^\circ$  and gave the following analytical result after drying in a vacuum desiccator :

0.1135 gave 0.2490  $\text{CO}_2$  and 0.0630  $\text{H}_2\text{O}$ .  $\text{C} = 59.83$ ;  $\text{H} = 6.17$ .

$\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS}$  requires  $\text{C} = 71.7$ ;  $\text{H} = 7.12$ ; and  $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS} \cdot \text{CHCl}_3$  requires  $\text{C} = 60.1$ ;  $\text{H} = 5.95$  per cent.

The salt therefore crystallises with a molecule of chloroform of crystallisation, which accounts for its indefinite melting point. On account of the slight solubility of the salt in water, its rotatory power was determined in 10 per cent. alcohol.

0.6944 in 50 c.c. gave  $\alpha_D = 0.464^\circ$  in a 400 mm. tube.  $[\alpha]_D = 8.35^\circ$  and  $[M]_D = 53.33^\circ$  (for  $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS} + \text{CHCl}_3$ ), and  $43.34^\circ$  (for  $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS}$ ).

The radicle  $\text{NPhMe}(\text{C}_7\text{H}_7)_2$  therefore appears to be inactive.

Since the salt separated with a molecule of chloroform, it was thought advisable to crystallise the substance from some other solvent and redetermine its rotatory power. A mixture of methylene diethyl ether and benzene was found to be a suitable solvent, and after several



crystallisations, the salt melted sharply at 139—141°, and when dried at 100° gave the following result on analysis:

0.1197 gave 0.3140 CO<sub>2</sub> and 0.0768 H<sub>2</sub>O. C=71.5; H=7.12.

C<sub>31</sub>H<sub>37</sub>O<sub>4</sub>NS requires C=71.7; H=7.12 per cent.

Determinations of the rotatory power were made by dissolving the salt in as little absolute alcohol as possible, and then making the solution up to a definite volume with water or dilute alcohol.

The sparing solubility of the salt makes the determinations difficult; the solutions, although dilute, being in many cases nearly saturated.

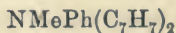
(I) 0.7735 in 50 c.c. gave  $\alpha_D = 0.561^\circ$  in a 400 mm. tube.  $[\alpha]_D = 9.06^\circ$ ;  $[M]_D = 47.0^\circ$ .

(II) 0.5536 in 50 c.c. gave  $\alpha_D = 0.457^\circ$  in a 400 mm. tube.  $[\alpha]_D = 10.3^\circ$ ;  $[M]_D = 53.5^\circ$ .

(IV) 0.3464 in 25 c.c. gave  $\alpha_D = 0.27^\circ$  in a 200 mm. tube (with a Landolt-Lippich three field polarimeter).  $[\alpha]_D = 9.75^\circ$ , and  $[M]_D = 50.6^\circ$ .

(V) 17.5 c.c. of the solution (IV) made up to 25 c.c. gave  $\alpha_D = 0.18^\circ$  hence  $[\alpha]_D = 9.28^\circ$  and  $[M]_D = 48.2^\circ$ .

These values are in sufficiently close agreement (allowing for the large experimental error) with the expected value  $51.7^\circ$  to show that the effect of the alcohol is not large, and that the radicle



is inactive. The iodide was precipitated from a dilute alcoholic solution of the camphorsulphonate by the addition of concentrated potassium iodide solution. After one crystallisation from alcohol, it melted at 134—135°, and, when examined in alcoholic solution, was quite inactive.

#### *Dibenzylmethylisobutylammonium Iodide.*

(1) Benzylisobutylamine, prepared as described by Wedekind, and methyl iodide in molecular proportion reacted rapidly and set to a solid mass, which was heated on the water-bath for some time, decomposed with caustic potash, the solution extracted with ether, and the ethereal extract dried over fused sodium sulphate. After evaporating off the ether, the oil was fractionated (under reduced pressure, when a very good yield of benzylmethylisobutylamine was obtained with a constant boiling point of 115—118° under 30 mm. pressure.

The base, when mixed with the theoretical quantity of benzyl iodide and allowed to remain in the cold for three weeks, yielded a red oil, which was twice dissolved in alcohol and precipitated by the

addition of ether, after which it crystallised when rubbed with a little alcohol. The salt, after repeated crystallisation from a mixture of alcohol and ethyl acetate, was obtained in colourless prisms melting sharply at 174—175°.

(2) Considerable difficulty was experienced in the preparation of dibenzylisobutylamine. When dibenzylamine (2 mols. and isobutyl bromide (1 mol.) were heated for about two hours on the water-bath, crystals separated, which, on filtering and washing with ether, were found to melt at 250°, and were therefore dibenzylamine hydrobromide (Carrara gives m. p. 250°). The liquid portion, when distilled under reduced pressure, yielded a first fraction distilling at 198—210° under 20 mm. pressure, which was found to be unchanged dibenzylamine (its hydrochloride was prepared, m. p. 256°). A very small quantity of oil then distilled over and partially solidified; the residue in the flask solidified completely. Both distillate and residue were pressed on a porous plate, and, when crystallised several times from light petroleum, yielded white needles melting at 92—93°.

(I) 0.1146 gave 0.3685 CO<sub>2</sub> and 0.0737 H<sub>2</sub>O. C = 87.6; H = 7.06.

(II) 0.1930 „ 8.3 c.c. moist nitrogen at 14.5° and 765 mm. N = 5.0.

(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>N requires C = 87.8; H = 6.9; N = 7.3 per cent.

The substance is therefore tribenzylamine, the melting point of which was given by Cannizzaro as 91.3°. This transformation is of interest from its similarity to the well known change which results from the action of methyl iodide on benzylaniline, in which dibenzylaniline is the chief product. A similar result was obtained when isobutyl iodide was used.

In order to avoid possible molecular transformation by the action of heat, a mixture of equivalent quantities of dibenzylamine and isobutyl iodide was left in the cold for several months. Crystals separated, which were undoubtedly dibenzylamine hydriodide, the oil was filtered off and mixed with methyl iodide. The crystalline product was drained and submitted to fractional crystallisation in the hope of separating any of the desired compound which might be present. The only substance which could be isolated was recrystallised from alcohol and ethyl acetate and then melted at 186—187.5°.

(I) 0.1444 gave 0.2867 CO<sub>2</sub> and 0.0744 H<sub>2</sub>O. C = 54.15; H = 5.72.

(II) 0.1598 „ 0.3179 CO<sub>2</sub> „ 0.0807 H<sub>2</sub>O. C = 54.31; H = 5.61.

N(C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>I requires C = 54.5; H = 5.67. NMe(C<sub>6</sub>H<sub>5</sub>)(C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>I requires C = 57.9; H = 6.6 per cent.

The product was therefore *dibenzylmethylammonium iodide*. The corresponding chloride has been obtained by Jackson and Wing (*Amer. Chem. J.*, 1887, 9, 80).

The action of benzyl chloride on benzylisobutylamine was then studied. On heating together either one molecule of each or one molecule of the chloride and two molecules of the base, some benzylisobutylamine hydrochloride separated; but the reaction was very incomplete, even after heating for several hours. On filtering and distilling the filtrate under reduced pressure, the liquid boiled over a very wide range, and obviously consisted of a mixture from which it was found impossible to separate any pure compound.

The desired result was finally attained by the action of benzyl iodide on isobutylamine. A mixture of two molecular proportions of the base and one of the iodide rapidly became very hot and a solid separated. After cooling, the odour of benzyl iodide could still be detected, so that to complete the reaction the mixture was heated for about an hour on the water-bath. The solid, after washing with ether several times, formed colourless, glistening plates, very soluble in alcohol and fairly so in ethyl acetate and water; it was readily decomposed by caustic potash.

After crystallisation from hot ethyl acetate, the compound melted at 165—166° and gave the following numbers:

0.6950 required 23.8 c.c. *N*/10 AgNO<sub>3</sub>. I = 43.5.

NH(C<sub>4</sub>H<sub>9</sub>)·C<sub>7</sub>H<sub>7</sub>, HI requires 43.6 per cent.

The solid is therefore benzylisobutylamine hydriodide and the liquid should be the required tertiary amine.

After distilling off the ether from the filtrate, the residual oil was fractionated three times under reduced pressure, after which the greater part boiled constantly at 170—173° under 10 mm. pressure.

The base, when mixed with one molecular proportion of methyl iodide, slowly deposited a red gum, which was purified and induced to crystallise in the foregoing manner. Small, colourless prisms were thus obtained, which were identical in appearance, melting point, and optical properties with those obtained by the first method. After drying in a vacuum desiccator, the following results were obtained:

(I) 0.1433 gave 0.3036 CO<sub>2</sub> and 0.0829 H<sub>2</sub>O. C = 57.8; H = 6.43.

(II) 0.1378 „ 0.2926 CO<sub>2</sub> „ 0.0795 H<sub>2</sub>O. C = 57.9; H = 6.41.

C<sub>19</sub>H<sub>26</sub>NI requires C = 57.87; H = 6.6.

(3) The same quaternary compound might also be produced by the union of dibenzylmethylamine and isobutyl iodide, but unfortunately it has not been found possible to produce the tertiary amine, since when dibenzylamine and methyl iodide are mixed in any proportion, even at low temperatures, a violent reaction takes place almost immediately with the production of the foregoing dibenzyltrimethylammonium iodide.



Dibenzylmethylisobutylammonium *d*-camphorsulphonate, prepared in the usual way, formed a colourless viscid mass, which, when kept in a desiccator, slowly became crystalline; the solid, however, crystallises badly from solvents, and is unsuitable for a long series of fractional crystallisations. All attempts to cause the *d*-bromocamphorsulphonate to crystallise have hitherto been unsuccessful, so that it has unfortunately not been possible to decide as to the activity of the radicle  $\text{NMe}(\text{C}_7\text{H}_7)_2\cdot\text{C}_4\text{H}_9$ , but there is no reason to believe that it would behave differently to the others which have been examined.

### *Cyclic Compounds.*

1-Methyl- $\alpha$ -picolinium *d*-camphorsulphonate was prepared by heating together molecular proportions of the corresponding iodide (m. p. 224—224.5°) and silver *d*-camphorsulphonate with ethyl acetate and a small quantity of alcohol. The salt, which crystallised readily in a vacuum desiccator, is sparingly soluble in ethyl acetate, slightly more so in acetone, and dissolves very readily in methylene diethyl ether; it was repeatedly crystallised from a mixture of acetone and ethyl acetate, and then from acetone, being obtained in long, colourless needles which melted constantly, but not very sharply, at 162—164°. The rotatory power of the salt, determined after successive crystallisations, was constant, but the values of  $[\text{M}]_D$  differed slightly from 51.7°, the discrepancy being very probably due to hydrolytic dissociation.

0.585 in 25 c.c. gave  $\alpha_D = 0.685^\circ$  in a 200 mm. tube;  $[\alpha]_D = 14.64^\circ$  and  $[\text{M}]_D = 49.6^\circ$ .

0.3450 gave 0.7550  $\text{CO}_2$  and 0.2290  $\text{H}_2\text{O}$ . C = 59.0; H = 7.37.

$\text{C}_{17}\text{H}_{25}\text{O}_4\text{NS}$  requires C = 60.1; H = 7.37 per cent.

1-Methyl- $\alpha$ -picolinium *d*-bromocamphorsulphonate, prepared in the same way as the camphorsulphonate, was found to crystallise readily; it is very sparingly soluble in acetone and ethyl acetate, but dissolves more freely in methylene ether. After repeated crystallisation from a mixture of ethyl acetate with a small amount of methylene ether, it was obtained in colourless needles melting at 186—187°.

The following determinations were made on a specimen dried in a vacuum desiccator.

0.527 in 25 c.c. gave  $\alpha_D = 2.72^\circ$ ;  $[\alpha]_D = 64.52^\circ$  and  $[\text{M}]_D = 270^\circ$ .

0.3337 gave 0.5900  $\text{CO}_2$  and 0.1745  $\text{H}_2\text{O}$ . C = 48.5; H = 5.81.

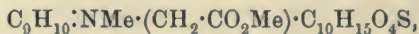
$\text{C}_{17}\text{H}_{24}\text{O}_4\text{NBrS}$  requires C = 48.8; H = 5.74 per cent.

The platinumchloride, when precipitated from a solution of the camphorsulphonate or bromocamphorsulphonate, formed bright orange

plates melting at 225—226°; it is extremely sparingly soluble in alcohol, ethyl acetate, acetone, methylene ether and epichlorohydrin. A solution of the hydrochloride prepared by the action of hydrogen sulphide on this salt suspended in warm water was inactive.

The radicle  $\text{NMe}:\text{C}_5\text{H}_4\text{Me}$ , although apparently devoid of a plane of symmetry, still seems unable to give rise to optical activity.

*Methyl kairolinium-1-acetate d-camphorsulphonate,*



was prepared by heating together molecular proportions of silver *d*-camphorsulphonate and Wedekind's methyl kairolinium-1-acetate iodide (*Annalen*, 1861, 118, 114). The salt, which crystallised in long prisms, was found to be rather sparingly soluble in ethyl acetate, but slightly more so in acetone; it was crystallised from ethyl acetate several times and then from a mixture of ethyl acetate and acetone, and the rotatory powers of several of the fractions were taken in aqueous solution with the Landolt-Lippich three-field polarimeter, using sodium light. The value of  $[\text{M}]_D$  gradually became constant at about 49.6° and did not attain the value for the acidic ion, 51.7°. The melting point of the salt was found to be 146.5—147°.

After the fourth crystallisation, 1.0380 in 35 c.c. gave  $\alpha_D = 0.65^\circ$  in a 200 mm. tube;  $[\alpha]_D = 10.96^\circ$  and  $[\text{M}]_D = 49.4^\circ$ .

After the eighth crystallisation, 0.9975 in 25 c.c. gave  $\alpha_D = 0.87^\circ$  in a 200 mm. tube;  $[\alpha]_D = 10.9^\circ$  and  $[\text{M}]_D = 49.2^\circ$ .

After the tenth crystallisation, 0.884 gave in 25 c.c.  $\alpha_D = 0.78^\circ$  in a 200 mm. tube;  $[\alpha]_D = 11.03^\circ$  and  $[\text{M}]_D = 49.7^\circ$ .

A specimen dried in a vacuum desiccator gave the following numbers:

0.1374 gave 0.3078  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}$ .  $\text{C} = 61.09$ ;  $\text{H} = 7.32$ .

$\text{C}_{23}\text{H}_{33}\text{O}_6\text{NS}$  requires  $\text{C} = 61.19$ ;  $\text{H} = 7.31$  per cent.

*Methyl kairolinium-1-acetate d-bromocamphorsulphonate*, which was prepared in the usual way, gradually solidified when left in a desiccator, and triturated with ether; when crystallised repeatedly from hot acetone, it formed stellate needles melting at 134—136°. The values obtained for  $[\text{M}]_D$  gradually rose to 263°, a value fairly near to that of 271°, calculated for the acidic ion.

After the fifth crystallisation, 0.477 in 25 c.c. gave  $\alpha_D = 1.87^\circ$  in a 200 mm. tube;  $[\alpha]_D = 49.0^\circ$  and  $[\text{M}]_D = 259.7^\circ$ .

After the eighth crystallisation, 0.597 in 25 c.c. gave  $\alpha_D = 2.37^\circ$  in a 200 mm. tube:  $[\alpha]_D = 49.6^\circ$  and  $[\text{M}]_D = 263^\circ$ .

A specimen gave the following result after drying in a vacuum desiccator:

0.1089 gave 0.2057  $\text{CO}_2$  and 0.0612  $\text{H}_2\text{O}$ .  $\text{C} = 51.5$ ;  $\text{H} = 6.23$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{NBrS}$  requires  $\text{C} = 52.0$ ;  $\text{H} = 6.04$  per cent.

The platinichloride, precipitated by the addition of an aqueous solution of chloroplatinic acid to an aqueous solution of the salt, was obtained as a dull yellow, crystalline powder melting at  $182\text{--}183^\circ$  with decomposition; it was very sparingly soluble in all ordinary solvents and also in methylene ether and epichlorohydrin. A solution of the hydrochloride prepared by the action of hydrogen sulphide on a suspension of the platinichloride in warm water was found to be inactive. It therefore appears that the radicle  $\text{C}_9\text{H}_{10}\text{:NMe}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Me}$  is inactive.

The results obtained with the above tetrahydroquinoline derivative are not very conclusive on account of the discrepancies between the observed values of  $[\text{M}]_D$  and those of the acidic ion, the deviations being greater than could be accounted for by experimental error. The examination of other derivatives, however, gave more satisfactory numbers.

*1-Methyl-1-ethyltetrahydroquinolinium d-bromocamphorsulphonate*, prepared from the corresponding iodide already described by Claus and Stegelitz (*Ber.*, 1884, 17, 1331), crystallised readily, and, after repeated crystallisation from acetone, was obtained in stellate aggregates of leaf-like crystals melting at  $161\text{--}161.5^\circ$ .

After the sixth crystallisation, 0.448 in 25 c.c. gave  $\alpha_D = 2.00^\circ$  in a 200 mm. tube;  $[\alpha]_D = 55.8^\circ$  and  $[\text{M}]_D = 271^\circ$ .

After the eighth crystallisation, 0.3844 in 25 c.c. gave  $\alpha_D = 1.71^\circ$ ;  $[\alpha]_D = 55.6^\circ$  and  $[\text{M}]_D = 270.2^\circ$ .

0.1268 gave 0.2513  $\text{CO}_2$  and 0.0726  $\text{H}_2\text{O}$ .  $\text{C} = 54.1$ ;  $\text{H} = 6.36$ .

$\text{C}_{22}\text{H}_{22}\text{O}_4\text{NBrS}$  requires  $\text{C} = 54.3$ ;  $\text{H} = 6.57$  per cent.

The camphorsulphonate of the base was obtained in a crystalline state, but the crystals were very apt to become gummy, and as the substance was not very suitable for a long series of fractional crystallisations it was not further examined.

The platinichloride separated in small, bright yellow prisms, which melted at  $192\text{--}193^\circ$  with decomposition; it was extremely sparingly soluble in all the ordinary solvents. A solution of the hydrochloride, prepared by the action of hydrogen sulphide on the platinichloride suspended in warm water, was found to be inactive. The radicle  $\text{C}_9\text{H}_{10}\text{:NMeEt}$  therefore appears to be inactive.

*1-Benzyl-1-ethyltetrahydroquinolinium iodide* was very readily formed from a mixture in molecular proportion of ethyltetrahydroquinoline and benzyl iodide, the mixture becoming solid after 24 hours; it was repeatedly dissolved in alcohol, ether added until a permanent turbidity



was produced, and the solution then left until crystals were deposited. The salt was thus obtained in stellate aggregates of almost colourless needles melting at 105—106°.

0.5682 gave 18.7 c.c. moist N at 16° and 768 mm.  $N = 3.89$ .

$C_{18}H_{22}NI$  requires  $N = 3.7$  per cent.

1-Benzyl-1-ethyltetrahydroquinolinium d-camphorsulphonate, prepared from the iodide, slowly became crystalline in the desiccator; it is very sparingly soluble in ethylacetate, slightly more so in acetone, and dissolves very readily in methylene ether. When crystallised repeatedly from a hot mixture of acetone (10 vols.) and methylene ether (1 vol.), the salt was obtained in short, colourless prisms melting at 164—165°. The value of  $[M]_D$  gradually rose towards the number for the acidic ion, namely, 51.7°.

After four crystallisations, 0.606 in 25 c.c. gave  $\alpha_D = 0.47^\circ$  in a 200 mm. tube;  $[\alpha]_D = 9.7^\circ$  and  $[M]_D = 46.8^\circ$ .

After ten crystallisations, 1.047 in 25 c.c. gave  $\alpha_D = 0.87^\circ$  in a 200 mm. tube;  $[\alpha]_D = 10.4^\circ$  and  $[M]_D = 50.2^\circ$ .

0.1042 gave 0.2670  $CO_2$  and 0.0730  $H_2O$ .  $C = 69.89$ ;  $H = 7.78$ .

$C_{28}H_{30}O_4NS$  requires  $C = 69.6$ ;  $H = 7.66$  per cent.

The corresponding d-bromocamphorsulphonate formed a gummy mass, which could not be induced to crystallise. The iodide recovered from an aqueous solution of the camphorsulphonate by the addition of concentrated potassium iodide solution was found to be quite inactive in solution in dilute alcohol. After recrystallisation from dilute alcohol, it was colourless and melted at 106°. The radicle  $C_9H_{10}:NEt \cdot C_7H_7$  therefore appears to be inactive.

### *The Optical Activity of Asymmetric Ammonium Compounds.*

The existence of optically active compounds, the activity of which is due entirely to the presence of an asymmetric nitrogen atom, was firmly established by Pope and Peachey (Trans., 1899, 75, 1127), and up to the present the *d*- and *l*- $\alpha$ -phenylbenzylmethylallylammonium salts isolated by them are the only optically active nitrogen compounds known. The author's object in examining these compounds was to determine: (1) whether compounds containing other radicles could also show this activity; (2) whether the phenomenon was in any way connected with the existence of inactive isomerides of the same compound or not, and hence to show that the absence of activity in compounds of the type  $NR'R''R'''_2X$  was not due to the mobility of the groups or the absence of inactive isomerides. The examination has been pursued with this object alone, so that the values

of the rotatory powers given in this paper must be regarded as being only approximate; a further account of these compounds will shortly be laid before the Society.

*Phenylbenzylmethylethylammonium iodide*, readily obtained by mixing molecular quantities of methylethylaniline and benzyl iodide, was crystallised repeatedly from warm alcohol and thus obtained in colourless needles melting at about  $145\text{--}146^\circ$  when quickly heated.

*Phenylbenzylmethylethylammonium d-camphorsulphonate* was obtained from the iodide in the usual manner; it was rather sparingly soluble in ethyl acetate and acetone, much more so in methylene ether, and was crystallised repeatedly from a mixture of about one volume of the latter solvent to four or five volumes of the former.

A few polarimetric determinations made on successive fractions after drying in a vacuum desiccator showed that the salt was being gradually resolved into two fractions of different rotatory powers, the salt of the dextrorotatory base being the less soluble.

After the third crystallisation (m. p.  $178\text{--}180^\circ$ ),  $[\alpha]_D = 13.8^\circ$ ,  $[M]_D = 63.2^\circ$ ; sixth crystallisation,  $[\alpha]_D = 14.9^\circ$ ,  $[M]_D = 68.1^\circ$ ; eighth crystallisation (m. p.  $181^\circ$ ),  $[\alpha]_D = 15.1^\circ$ ,  $[M]_D = 69.0^\circ$ .

0.2260 gave 0.565  $\text{CO}_2$  and 0.1585  $\text{H}_2\text{O}$ . C = 68.2; H = 7.78.

$\text{C}_{20}\text{H}_{25}\text{O}_4\text{NS}$  requires C = 68.2; H = 7.66 per cent.

*d-Phenylbenzylmethylethylammonium iodide* was precipitated in small, colourless prisms on mixing strong solutions of potassium iodide and the camphorsulphonate. After recrystallisation from rectified spirit in the dark, the salt melted at  $146\text{--}147^\circ$ , and in alcoholic solution gave  $[\alpha]_D = 5.24^\circ$  and  $[M]_D = 18.5^\circ$ .

Another preparation obtained from the camphorsulphonate after eight crystallisations gave the following result:

0.562 in 25 c.c. alcohol gave  $\alpha_D = 0.35^\circ$  in a 200 mm. tube,  $[\alpha]_D = 7.8^\circ$ ;  $[M]_D = 27.5^\circ$ .

0.1334 gave 0.2650  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ . C = 54.2; H = 5.80.

$\text{C}_{16}\text{H}_{20}\text{NI}$  requires C = 54.4; H = 5.66 per cent.

The great difference between the value of  $[M]_D$  for this salt and that for the compound resolved by Pope and Peachey, owing to the replacement of the allyl radicle by ethyl, is very striking.

The more soluble portion of the camphorsulphonate could not be obtained pure, and it will be necessary to use *l*-camphorsulphonic acid for the isolation of the *l*-rotatory isomeride.

*Phenylmethylethylallylammonium d-bromocamphorsulphonate*, when prepared from the corresponding iodide  $[\text{NMeEtPh}(\text{C}_6\text{H}_5) \cdot \text{I} + \text{CHCl}_3]$ , described by Wedekind, crystallised readily from ethyl acetate in colourless prisms melting at  $134\text{--}135^\circ$ ; it was repeatedly crystallised

from ethyl acetate and then from acetone. Successive fractions were used for determinations of rotatory power and the values obtained gradually increased until the value  $[M]_D = 293^\circ$  was reached.

The corresponding platinichloride was precipitated as a dull yellow, crystalline powder on adding chloroplatinic acid to an aqueous solution of the bromocamphorsulphonate. It is extremely sparingly soluble in all the ordinary organic solvents, and even in epichlorohydrin, so that a determination of its rotatory power was impossible; a weak solution of the hydrochloride obtained by suspending the double salt in warm water and treating with hydrogen sulphide had a decided, although slight, dextrorotation. The platinichloride decomposed at  $159-160^\circ$ .

0.5296 gave 0.134 Pt.  $Pt = 25.3$ .

$(C_{12}H_{18}N)_2PtCl_6$  requires  $Pt = 25.5$  per cent.

The isomerides of the quinquivalent nitrogen compounds,  $NR'R''R'''X$ , which were to be expected, on the basis of any possible configuration for the nitrogen atom (compare p. 1401), do not appear to be capable of existence, and the one compound which is always formed has the planisymmetric configuration (VII), since it cannot be resolved into optically active forms. The formation of the same compound from  $NR'R''R'''$  and  $R'''X$  and from  $NR'R''R'''$  and  $R''X$  is explained by assuming an intramolecular transformation of the initial additive product.



VII.

The non-existence of optical activity is not due to the mobility of the groups, since the salts of phenylbenzylmethylethylammonium hydroxide and phenylmethylethylallylammonium hydroxide are optically active, although the groups in the latter case have the lowest molecular weight possible in compounds of this class.

Derivatives of pyridine and tetrahydroquinoline which apparently contain an asymmetric nitrogen atom do not seem to be capable of resolution into optically active forms.

The author desires to express his gratitude to Professor Dewar for placing at his disposal the excellent polarimeter used in these



experiments and to Professor W. J. Pope for his kindness in reading this paper in manuscript form.

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### CXXXVIII.—*The Molecular Formulæ of Fused Salts as Determined by their Molecular Surface Energy.*

By J. FRANK BOTTOMLEY, Ph.D.

FUSED salts, like solutions of salts in water, are known to be good conductors of electricity, but inasmuch as a fused salt is physically homogeneous, it must be concluded, if the ionic hypothesis is accepted, that a portion of the salt acts as a solvent, and exerts an ionising action on another portion. Liquids which show an ionising action are without exception those consisting of complex molecules; and it was to be expected that the molecular weights of fused salts would be considerably greater than those implied by their simple formulæ. It was suggested by Sir William Ramsay that an investigation of the molecular complexity of molten salts would be of considerable interest, and that the method of Ramsay and Shields\* would probably be applicable. For non-associating liquids, the variation of molecular surface energy is a rectilinear function of the temperature, expressible by the equation

$$d\{\gamma(Mv)^{\frac{1}{3}}\}/dt = k,$$

where  $\gamma$  is the surface energy measured in dynes, and  $(Mv)^{\frac{1}{3}}$  the molecular surface measured in square centimetres. The average value of  $k$  was found to be 2.121.

For associating liquids, on the other hand, the value of  $k$  is less than the constant, 2.12, and, as Ramsay pointed out in a later paper,† it is possible to estimate very approximately the number of molecules which associate to form a complex. But in the present instance the measurements are not sufficiently numerous or correct to make it possible to utilise the more correct equation; hence the simpler one,  $x = \left\{\frac{2.12}{k}\right\}^{\frac{1}{3}}$ , has been employed. In this expression, the variation of the factor of

\* *Phil. Trans.*, 1893, 184, 647.

† *Proc. Roy. Soc.*, 1894, 56, 175.

association with the temperature has been neglected. Moreover, it was sufficient for the purpose in view to determine whether or not the fused salts consisted of complex molecular groupings.

The capillary constants of a large number of fused salts have already been determined by Quincke by his ingenious drop method, but that process did not seem to be applicable in this case, for it was necessary to determine the values at known temperatures. The capillary constants were therefore calculated from the rise of the fused salts in capillary tubes, and for this reason the investigation was restricted to salts which could be safely fused in glass vessels.

Measurements of the capillary rise were attempted with lithium, sodium, potassium, and silver nitrates, potassium chlorate and dichromate, and zinc and stannous chlorides, but, although much time was spent on the experiments, successful results were attained only in the case of the nitrates of potassium and sodium. Lithium nitrate attacks Jena glass, even at  $260^{\circ}$ , producing a curious opalescent appearance and rendering it opaque; silver nitrate decomposes at  $260^{\circ}$  and blackens glass; potassium chlorate also decomposes and gives off a slow stream of bubbles, which made readings in a capillary tube impossible; potassium dichromate turns nearly black on melting, and this renders accurate measurements impossible; zinc chloride, which has a treacherous consistence, exhibits a considerable capillary rise. Stannous chloride held out better prospects, for it melts to a clear liquid; but on continued fusion it became turbid, and measurements of its surface tension could not be made.

#### *Description of the Apparatus and Details of the Experiments.*

In order to determine the variation of molecular surface energy with temperature, it is necessary to measure the capillary rise and to ascertain the density of the fused salt at known temperatures. But owing to the high temperature at which most inorganic salts fuse, the method employed by Ramsay and Shields had to be considerably modified. In the first place, it was necessary to maintain temperatures of over  $300^{\circ}$  by means of a bath of some transparent material, and for this purpose a Jena glass beaker containing fused sodium nitrate was found suitable. Whereas ordinary glass, either hard or soft, becomes opaque, the glass supplied by Messrs. Schott and Genossen, when heated for days with the fused nitrates of sodium or potassium, remains perfectly transparent and shows no sign of being attacked.

The bath consisted of a Jena glass beaker containing about a kilogram of recrystallised sodium nitrate, heated over a large Fletcher's burner; the liquid was agitated with a brass stirrer, rotated by a small

hot-air engine. A long lever was soldered to the tap of the burner, and it was found that with a little care the temperature of the bath could be kept constant to within a degree for a considerable time.

The temperature of the bath was measured with a boro-silicate glass thermometer, which read up to 500°.

The capillary tubes were drawn from Jena glass combustion-tubing fused in an oxygen blow-pipe in lengths of several yards; the central parts of these long pieces were then cut up into short lengths, both ends of which were measured under a microscope, fitted with a micrometer eye-piece, and compared with a standard millimeter, divided into hundredths. Great care was taken in selecting the tubes, and only those which were round and which showed very little difference between the two ends were accepted. This was necessary, for the same tube could not be used over again as in Ramsay and Shield's experiments, and it was not always possible to make the measurements near the top of the tube.

The salt, the surface tension of which was to be measured, was introduced as a fine powder into a tube of soft Jena glass provided with a narrower side-tube in connection with a Tüpler pump; the tube was immersed in a small bath of sodium nitrate and melted, when a measured capillary tube, attached by means of fine platinum wire to a long platinum rod, was lowered into the liquid, and the tube was stoppered and exhausted. It is exceedingly difficult to remove all air-bubbles from the capillary tube, and the only way of effecting this was by alternately exhausting the apparatus and allowing air to rush in about a dozen times. When this had been done successfully, the stopper was removed, and the tube was transferred to the constant temperature bath, the temperature of which had meanwhile been adjusted. A glass scale, illuminated from behind with an electric light, was fixed in front of the apparatus, and the height of the liquid was read by aid of a telescope fitted with an ocular micrometer.

The densities of the fused salt were determined by sucking it up into pipettes of Jena glass with capillary stems, the upper one of which was marked with a fine etched line. The pipettes were calibrated by weighing with water. During each experiment, a Jena glass test-tube containing the salt was kept in the constant temperature bath, and after each measurement of the capillary rise, two or three pipettes were filled by sucking the fused salt up to the mark on the stem; care was taken to allow the stem to warm up first, as otherwise the salt tends to solidify in the capillary portion.



*Determinations of the Capillary Rise of Sodium and Potassium Nitrates.*

In the tables given below, the letters have the following meaning :

|                                   |  |
|-----------------------------------|--|
| $M$ = molecular weight.           | $h$ = rise in the capillary tube (centimetres).          |
| $v$ = specific volume.            | $r$ = radius of capillary tube.                          |
| $g = 981.1$ .                     | $\gamma$ = surface-tension in dynes = $\frac{1}{2}$ ghr. |
| $\rho$ = density of fused salt.   | $t$ = temperature in degrees centigrade.                 |
| $x$ = coefficient of association. |  |

Potassium nitrate ; I.  $r = 0.02301$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 338°  | 5.215 | 1.867    | 109.8      | 1571                   | 0.471 | 9.55  | 101   |
| 406   | 5.149 | 1.820    | 105.8      | 1539                   | —     | —     | —     |

Potassium nitrate ; II.  $r = 0.02763$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 349°  | 4.20  | 1.869    | 106.4      | 1521                   | 0.554 | 7.49  | 101   |
| 414   | 4.163 | 1.764    | 100.7      | 1485                   | —     | —     | —     |

Potassium nitrate ; III.  $r = 0.02696$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 341°  | 4.39  | 1.867    | 106.4      | 1551                   | 0.485 | 9.145 | 101   |
| 407   | 4.34  | 1.814    | 104.6      | 1519                   | —     | —     | —     |

Sodium nitrate ; I.  $r = 0.02930$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 339°  | 3.92  | 1.891    | 106.4      | 1374                   | 0.500 | 8.73  | 85    |
| 405   | 3.64  | 1.844    | 101.8      | 1308                   | —     | —     | —     |

Sodium nitrate ; II.  $r = 0.02904$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 329°  | 4.103 | 1.895    | 110.8      | 1398                   | 0.381 | 13.13 | 85    |
| 405   | 4.05  | 1.846    | 106.5      | 1369                   | —     | —     | —     |

Sodium nitrate ; III.  $r = 0.02429$ .

| $t$ . | $h$ . | $\rho$ . | $\gamma$ . | $(Mv)^{\frac{2}{3}}$ . | $k$ . | $x$ . | $M$ . |
|-------|-------|----------|------------|------------------------|-------|-------|-------|
| 344°  | 4.94  | 1.886    | 111.0      | 1403                   | 0.453 | 10.17 | 85    |

From these results, it will be seen that the nitrates of both sodium and potassium are composed of complex molecules ; the average value of  $k$  for the former is 0.445, and for the latter, 0.503 ; these give for the molecular complexity the values 10.68 and 8.73 respectively. These values are undoubtedly too high ; still, it may be taken as certain that the molecules of fused nitrates are considerably more complex than are those represented by the simple formulæ. It may therefore be supposed that the molecules which are in the ionised state are protected by complex molecules from discharging into each other, and regenerating the non-ionised salt, in the same manner as the ions of such a salt as sodium chloride are protected by water molecules from combining to form molecules of sodium chloride.

In spite, therefore, of the paucity of results, it may be assumed that the conductivity of fused salts is to be explained on the same hypothesis as that which furnishes an explanation of the conductivity of solutions, namely, that in order to prevent the equalisation of potential of the ionic charges, a protective menstruum is necessary, and it appears that this menstruum may be furnished by the same substance as that which also undergoes ionisation.

### CXXXIX.—*Studies on Comparative Cryoscopy. Part I. The Fatty Acids and their Derivatives in Phenol Solution.*

By P. W. ROBERTSON, Sir George Grey Scholar.

ALTHOUGH Biltz showed that the change of molecular weight with concentration for the alcohols in benzene solution diminishes regularly as the homologous series is ascended (*Zeit. physikal. Chem.*, 1899, 29, 255), no similar relationship has been observed for other series of compounds. Having found that acetic and propionic acids associate in phenol solution,\* I was led to make a comparative examination of the members of this series and to study the influence of constitution on the change of association for a given range of concentration ( = "rate" of association).

#### *Method of Experiment and Calculation of Results.*

The molecular weights of the compounds under examination were determined by Raoult's method. The ordinary Beckmann's apparatus was employed, the thermometer being read to hundredths of a degree. Preliminary observations showed that concordant determinations of the freezing point were obtainable for pure phenol as well as for mixtures; moreover, it was ascertained that the amount of moisture absorbed was not sufficient to vitiate the results.

In one experiment, 10 to 20 grams of phenol were weighed into the apparatus and two readings of the freezing point were made; a sufficient amount of the foreign substance was now introduced to cause a depression of about  $0.7^{\circ}$ , and, after complete solution, a double determination of the temperature of solidification was performed, which was repeated six or seven times with fresh quantities of solute, providing that this substance was sufficiently soluble. When the dissolved substance was only slightly soluble, it was added in smaller

\* Paternò has pointed out that formic, acetic, and valeric acids associate in phenol, but did not examine the phenomenon from a quantitative standpoint (*Gazzetta*, 1896, 26, ii, 363).

quantities, and, consequently, in such cases the accuracy of the result could not be so great. The purity of the compounds employed was ascertained by melting or boiling point determinations, and comparative experiments showed that small quantities of impurities had little effect on the "rate" of association.

The molecular depression is calculated for each addition in the usual way. The reciprocals of the numbers thus obtained show the "rate" of association, which, after a fall of  $1^{\circ}$  in freezing point, is practically regular for several degrees. The percentage amount of change is now calculated over a range of  $3.5^{\circ}$ . This value is obtained by dividing the mean molecular depression of phenol (70) by 20, the fraction ( $\Delta/20$ ) being chosen for the following reasons:—

(1) To allow of a comparison being made between the "rate" of association of a given compound in different solvents. (2) Limited solubility in many cases prevents the attainment of a greater depression. (3) For greater depressions, Raoult's law is less accurate, and the molecular depression will then be influenced by causes other than association. (4) This represents the mean depression obtained in a series of experiments.

The constant representing the amount of change in molecular weight between certain limits will be denoted by the letter A. This constant is the percentage change of the reciprocal of the molecular depression of any substance in a solvent for successive additions of the substance over a range of  $\Delta/20$  degrees (where  $\Delta$  is the mean molecular depression of the solvent). The value of A may be negative; this shows that the molecular weight diminishes with the concentration.

Two examples will suffice to give a clear indication of the method of calculation.

*iso*Nitrosovaleric Acid ( $M = 131$ ).

| Weight of phenol. | Weight of acid. | $\Delta t$ . | Molecular depression. |
|-------------------|-----------------|--------------|-----------------------|
| 10.5              | 0.1654          | 0.795°       | 66                    |
| "                 | 0.2428          | 1.01         | 57.5                  |
| "                 | 0.1312          | 0.535        | 56                    |
| "                 | 0.1618          | 0.60         | 51                    |
| "                 | 0.1472          | 0.51         | 47.5                  |
| "                 | 0.1994          | 0.65         | 45                    |

$\therefore$  association increases  $1/57.5 - 1/45$  for a fall of  $(1.01/2 + 0.53 + 0.60 + 0.51 + 0.65/2) = 2.47^{\circ}$ .

$\therefore$  " " 39 per cent. for a fall of  $3.5^{\circ}$ .

|  |      |  |         |
|--|------|--|---------|
| Second series, $A = 35$                  | } 37 | $\Delta_1$ (molecular depression) = 65 | } 63.5. |
| The same acid recrystallised, $\Delta_1$ |      | " = 63                                 |         |
|  |      | " = 63                                 |         |



a Chlorophenylacetic Acid ( $M = 170$ ).

| Weight of phenol. | Weight of acid. | $\Delta t$ . | Molecular depression. |
|-------------------|-----------------|--------------|-----------------------|
| 11.8              | 0.1024          | 0.37°        | 72                    |
| "                 | 0.2328          | 0.805        | 69.5                  |
| "                 | 0.1768          | 0.63         | 71                    |
| "                 | 0.2134          | 0.76         | 71.5                  |
| "                 | 0.1746          | 0.60         | 69                    |
| "                 | 0.2192          | 0.765        | 70                    |

By a slight interpolation,  $A = 2.5$  }  $\Delta_1 = 70.5$  }  
 Second series,  $A = 3$  } 3  $\Delta_1 = 71$  } 71.

The remaining experimental results are collected in Table I (p. 1428). In addition to the values of  $A$ , the initial molecular depressions for a fall of  $1^\circ$  ( $\Delta_1$ ) are also calculated and shown in the table. At this low concentration, the association is in most cases only slight, and, consequently, the deviation of  $\Delta_1$  from the mean shows the irregularity of the solutes due to causes other than association.

In figures 2 and 3, the behaviour of a number of acids is represented diagrammatically, with the molecular depressions as ordinates and the temperatures as abscissae. Thus, if phenol freezes at  $40^\circ$ , and the molecular depression found when the freezing point of a mixture falls from  $38^\circ$  to  $37^\circ$  is 68, then this value is plotted against  $2.5^\circ$  (compare the foregoing calculation of results).

*The Relationship between Constitution and the "Rate" of Association.*

The different acids will be considered under the following divisions: (1) the fatty acids. (2) The mono-, di-, and tri-substituted acetic acids, where the substituents are phenyl, alkyl, and halogen radicles. (3) The dicarboxylic acids. (4) Hydroxy- and isonitroso-acids. (5) The substituted amino-acids. (6) Acids, the molecular depression of which increases with the concentration ( $A$  has a negative value). (7) Acids with an ethylenic linking. (8) Acids which decompose in the presence of phenol.

1. (a) *The Normal Fatty Acids* (Nos. 1—11, Table I, Fig. 1).

The change of association with the concentration alternately increases and decreases as the series is ascended, each of the members of the even series associating to a greater extent than either of the

TABLE I.

| Acid.                                  | A.  | Molecular depression<br>for 1° ( $\Delta_1$ ). |
|--|-----|--|
| 1. Acetic (C <sub>2</sub> ).....       | 23  | 71   |
| 2. Propionic (C <sub>3</sub> ) .....   | 13  | 70   |
| 3. Butyric (C <sub>4</sub> ) .....     | 14  | 69   |
| 4. Valeric (C <sub>5</sub> ) .....     | 11  | 67.5   |
| 5. Hexoic (C <sub>6</sub> ) .....      | 12  | 67   |
| 6. Heptoic (C <sub>7</sub> ).....      | 9   | 66   |
| 7. Caprylic (C <sub>8</sub> ).....     | 15  | 68   |
| 8. Capric (C <sub>10</sub> ) .....     | 28  | 67   |
| 9. Lauric (C <sub>12</sub> ) .....     | 42  | 64   |
| 10. Palmitic (C <sub>16</sub> ) .....  | 80  | 68   |
| 11. Stearic (C <sub>18</sub> ).....    | 98  | 70.5   |
| 12. <i>iso</i> Valeric .....           | 17  | 72.5   |
| 13. <i>iso</i> Butyric.....            | 9   | 69   |
| 14. Methylthylacetic .....             | 8   | 72.5   |
| 15. Chloroacetic .....                 | 14  | 71   |
| 16. Bromoacetic.....                   | 12  | 72   |
| 17. Phenylacetic.....                  | 14  | 69   |
| 18. Phenylpropionic .....              | 14  | 70   |
| 19. Bromobutyric .....                 | 8   | 77   |
| 20. Bromopalmitic.....                 | 66  | 80   |
| 21. $\alpha$ -Chlorophenylacetic ..... | 3   | 71.5   |
| 22. Trichloroacetic.....               | 2   | 68   |
| 23. Ethylmalonic .....                 | 31  | 72   |
| 24. Methylsuccinic.....                | 47  | 66   |
| 25. Sebacic .....                      | 16  | 70   |
| 26. Dibromomethylsuccinic .....        | 11  | —  |
| 27. Lactic .....                       | 16  | —  |
| 28. Mandelic .....                     | 22  | 70   |
| 29. Benzilic.....                      | 5   | 69.5   |
| 30. Hydroxydiphenylacetic .....        | 4   | 82   |
| 31. Dihydroxystearic.....              | 7   | 78   |
| 32. <i>iso</i> Nitrosovaleric .....    | 37  | 63.5   |
| 33. Phenylaminoacetic .....            | 17  | 69.5   |
| 34. Hippuric .....                     | -14 | 72.5   |
| 35. Phenylaminophenylacetic .....      | -16 | 80   |
| 36. Lævulic.....                       | -2  | 82   |
| 37. Cinnamic .....                     | 17  | 69   |
| 38. Oleic .....                        | 39  | 75   |

contiguous members of the odd series.\* If the acids of the even series are considered, it is found that the constant A slowly decreases to a

\* This alternate rise and fall was not noticed by Biltz for the "rate" of association in the case of the alcohols in benzene solution. It is noteworthy, however, that neither the melting points nor the differences of the boiling points of these compounds show an analogous behaviour to that of the fatty acids,

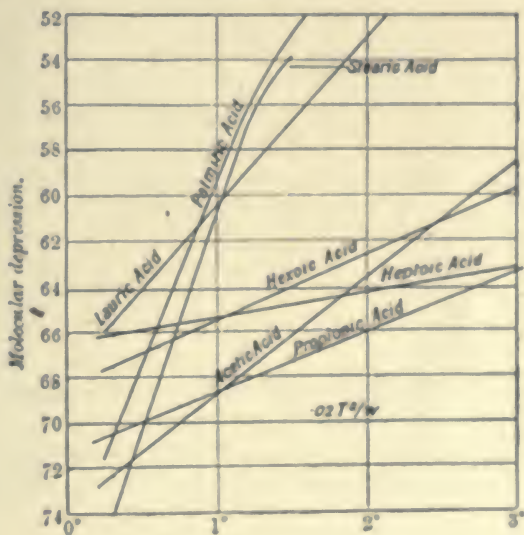
minimum at the  $C_8$  acid, and then increases more and more rapidly until finally the acids become too insoluble to be examined. The rapid association of the higher members of the series does not appear to be due to the carboxylic group, as in the case of the earlier acids, but to the hydrocarbon portion of the molecule.

The main grounds for this conclusion are as follows:

(i) Experiments have shown that the hydrocarbons themselves associate rapidly in phenol solution.

(ii) The ethereal salts of the lower fatty acids, in common with most compounds of this nature, have a negative value for  $A$ . But ethyl laurate and ethyl palmitate associate rapidly, and the association is greater for the compound containing the longer carbon chain.

FIG. 1.



(iii) Amongst the lower fatty acids, butyric acid, for example, the introduction of a bromine atom into the  $\alpha$ -position reduces  $A$  to about half its original value; higher up the series, this is not the case,  $\alpha$ -bromopalmitic acid associating almost as much as palmitic acid itself.

(iv) The introduction of an ethylenic linking in stearic acid breaks the continuity of the hydrocarbon chain, and the "rate" of association is considerably reduced.

This alternate rise and fall in the value of a physical constant as a series is ascended is of comparatively rare occurrence and, as in the present case, the constants of each series exhibit a minimum value. The melting points of the fatty acids constitute the best known

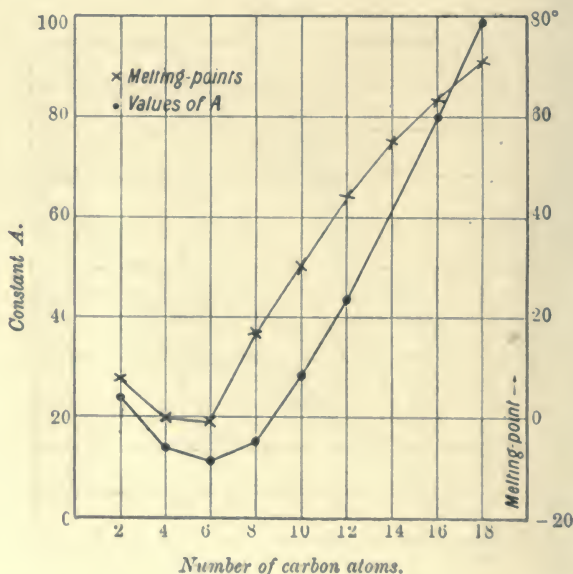


instance of this phenomenon (Baeyer, *Ber.*, 1877, 10, 1286). The striking similarity between the curves for the melting point and those for the "rate" of association in the case of the even members is shown in the accompanying diagram.

It is particularly interesting to notice that the two minima are exhibited by the same acid. Such a similarity suggests that the rise in the melting points as the series is descended from hexoic to acetic acid is directly due to molecular association.

The question then arises, why does the minimum value of the constant A occur at the sixth member of the series? Assuming with Baeyer (*Ber.*, 1885, 18, 2278) that a chain of five carbon atoms bends

FIG. 2.



on itself, the end of the carbon chain in the  $C_6$  acid would be in close proximity to the carboxyl group. This might hinder the union of the carboxyl radicles and thus prevent association. After the minimum has been reached, the whole molecule behaves physically as though it were a hydrocarbon, an increase in the length of the chain causing an increase in the "rate" of association.

A phenomenon of this nature has never previously been discussed, although Auwers has recorded a somewhat similar instance (*Zeit. physikal. Chem.*, 1900, 32, 39). *p*-Hydroxybenzaldehyde associates strongly in naphthalene solution owing to the influence of the hydroxyl group. The methyl derivative, *p*-hydroxyacetophenone, is less abnormal; the

abnormality now increases with the molecular weight of the ketone until *p*-hydroxypalmitophenone is reached, which associates to the same extent as the aldehyde. Here it is evident that the association is increased owing to the action of the hydrocarbon chain, just as in the case of the higher fatty acids in phenol solution.

A hydrocarbon chain, however, does not always exert this influence, for Biltz (*loc. cit.*) has shown that the "rate" of association of the alcohols in benzene decreases uniformly with the rise in molecular weight, even in the case of the extreme members of the series. Again, according to Auwers (*Zeit. physikal. Chem.*, 1897, 23, 449), the anilides of the fatty acids exhibit a similar behaviour in naphthalene solution.

### (b) *The Isomeric Fatty Acids.*

When the chain branches beyond the  $\alpha$ -carbon, the "rate" of association increases; this is seen in the case of *isovaleric* acid, the factor (17) of which is considerably greater than that of the corresponding normal acid (11). Substitution of the  $\alpha$ -hydrogen atom, on the other hand, decreases the "rate" of association. *iso*Butyric and methylethylacetic acids associate less rapidly ( $A = 9$  and 8 respectively) than *n*-butyric (14) and valeric acids (11). That this behaviour is general is confirmed by the results obtained for other disubstituted acids, which are discussed under division 2. By analogy, the magnitude of  $A$  should be still less for the trisubstituted acids (trichloroacetic acid,  $A = 2$ ).

If, as is probable, these results are only particular instances of a general law, this method, which could be employed in discriminating between the isomeric aliphatic acids, compares favourably with chemical processes in being quickly carried out with small quantities of material.

### 2.\* (a) *Monosubstituted Acetic Acids.*

In these compounds, the methyl, ethyl, phenyl, and benzyl groups and the halogen radicles have practically the same influence, reducing the constant  $A$  from 23 in the case of acetic acid to 12–14.

### (b) *Disubstituted Acetic Acids.*

Here, again, the halogens and the alkyl radicles of lower molecular weight exert the same influence, the resulting acid having the constant  $A = 8$ –9, although in the monosubstituted acids phenyl behaves like other groups, but the disubstituted acids containing this radicle

\* An acid of each type is represented in Fig. 3, p. 1432.

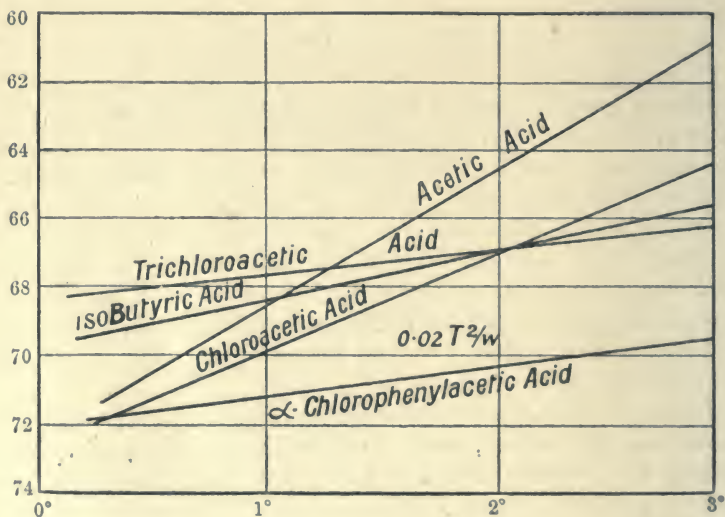
give normal values for  $A$ ; for example, the constant  $A$  of  $\alpha$ -chlorophenylacetic acid is 3, whilst that of hydroxydiphenylacetic acid is practically the same ( $A = 4$ ).

This peculiar behaviour of the phenyl radicle is not exhibited in the  $\beta$ -position.  $\beta$ -Phenylpropionic acid associates to the same extent as the other monosubstituted acetic acids.

(c) *Trisubstituted Acetic Acids.*

As might be expected, the constant  $A$  for trichloroacetic acid is approximately normal, that is, the association has almost disappeared

FIG. 3.



( $A = 2$ ). The only other acid of this class is benzilic acid, the constant ( $A = 5$ ) for which is probably increased owing to the action of the hydroxyl group.

3. *The Dicarboxylic Acids.*

These compounds, as well as the tricarboxylic acids, with their halogen and hydroxyl derivatives, are characterised by their sparing solubility in phenol. On introducing an alkyl group, however, the solubility is increased, so that these derivatives could in most cases be investigated (see under "Solubilities," p. 1438).

The addition of a carboxyl group always increases the "rate" of association, its action being greater than that of any other group hitherto studied. As in the monocarboxylic acids, the isomerides with



the largest number of hydrogen atoms in the  $\alpha$ -position have the highest association factor. This is made clear by comparing the isomeric ethylmalonic and methylsuccinic acids, the latter of which has the highest constant, the values being 31 and 47 respectively. Again, substitution of the  $\alpha$ -hydrogen atoms reduces the value of  $A$ , as in the case of  $\alpha\alpha'$ -dibromo- $\alpha$ -methylsuccinic acid, the constant for which is 11.

Here it is interesting to note that  $A$  is merely additive and can be calculated by the addition of the values characterising each of the carboxyl groups supposing that the other was absent. Calling  $a_1$  the fraction of the constant  $A$  due to the isocarboxylic group, and  $a_2$  that for the second group:  $A = a_1 + a_2 = 8 + 2 = 10$ , which is practically the same as the experimental result.

In the case of methylsuccinic acid,  $A = a_1 + a_2 = 8 + 14 = 22$ , but here the calculated value of the constant is far short of the experimental result, namely, 47. Hence it is probable that there is some mutual influence between the two groups, which becomes greatly increased with the increase in strength of one of them. The slight amount of association exhibited by sebacic acid ( $A = 16$ ) shows that at the end of a chain of eight carbon atoms the mutual influence is practically nil.

#### 4. *Hydroxy- and isoNitroso-acids.*

In phenolic solution, the molecular depressions of hydroxyl compounds tend to increase with the rise in concentration, that is,  $A$  is negative. Hence, the natural conclusion is that a hydroxy-acid would associate less rapidly than the acid from which it is derived. But this is not always the case. Indeed, the introduction of hydroxyl into the  $\alpha$ -position with respect to carboxyl raises the value of  $A$ . Such an increase is all the more remarkable, as most other substituents in the same position have an opposite effect. This result may be due to some mutual influence between the two groups, similar to that indicated in the case of the dicarboxylic acids.

It is interesting to compare lactic and mandelic acids with the acids from which they are derived.

|  | $A$ |   | $A$ |
|--|-----|---|-----|
| $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$          | 13  | $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$          | 16  |
| $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ | 14  | $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ | 22  |

The greater magnitude of the increase in the case of mandelic acid is especially noteworthy when it is remembered that disubstituted acids containing a phenyl radicle are characterised by their extremely low values of  $A$ . That the rapid association of mandelic acid is connected with the remaining  $\alpha$ -hydrogen atom is apparent from the fact

that benzilic acid, in which this hydrogen is replaced by phenyl, has a constant  $A = 5$ .

The two hydroxydiphenylacetic acids associate only slowly, the hydroxy-group exerting only a slight influence in both cases.

The introduction of two hydroxyl groups into the stearic acid molecule reduces the constant  $A$  from 98 to 7. But it must be borne in mind that the extensive association of stearic acid has been shown to be due to the influence of the hydrocarbon portion of the molecule.

*iso*Nitrosovaleric acid,  $\text{CH}_3 \cdot \text{C}(\text{NOH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is characterised by its rapid change of association with concentration, the entrance of the *isonitroso*-group into the valeric acid molecule causing the constant  $A$  to increase from 11 to 37. In order to ascertain the behaviour of the oximino-radicle alone, acetoxime was examined with the following result:  $A = -3$ ;  $\Delta_1 = 72.5$ . This does not explain why *iso*-nitrosovaleric acid has this large variation of association. The true explanation is, however, simple; the association is not caused either by the union of carboxyl radicles or by the combination of hydrocarbon chains, but is brought about by the junction of the carboxyl radicle of one molecule with the *isonitroso*-group of the next. For, if this is possible, other acids, acetic, for example, should associate with acetoxime in phenolic solution. The following experimental data show that this is undoubtedly the case.

A solution of acetoxime in 12.6 grams of phenol causing a depression of  $3.5^\circ$ .

| Weight of acetic acid added. | $\Delta t.$  | Molecular depression. |
|------------------------------|--------------|-----------------------|
| 0.0680                       | $0.45^\circ$ | 50                    |
| 0.0974                       | $0.735$      | 56                    |
| 0.1092                       | $0.81$       | 55                    |
| 0.1022                       | $0.775$      | 57                    |
| 0.1666                       | $1.21$       | 54.5                  |

A solution of toluene in 13.25 grams of phenol causing a depression of  $2^\circ$ .

| Weight of acetic acid added. | $\Delta t.$  | Molecular depression. |
|------------------------------|--------------|-----------------------|
| 0.0820                       | $0.77^\circ$ | 74.5                  |
| 0.1206                       | $1.10$       | 72.5                  |
| 0.1152                       | $1.01$       | 70                    |

When the acetoxime is present, the molecular depression is abnormally low, showing that the acid molecule has united with the oxime to form a complex. The fact that the values of  $\Delta$  increase with the concentration points in the same direction. When the amount of acetic acid added exceeds a molecular proportion,  $\Delta$  begins to decrease in value owing to the association of this acid alone.

In the presence of toluene, however, which does not unite with the acetic acid to form a molecular complex, the depression is large at first and decreases regularly as the solution becomes more concentrated.

### 5. *Substituted Amino-acids.*

The  $\alpha$ -amino-acids themselves could not be examined owing to their sparing solubility in phenol. Interesting results were obtained, however, from the investigation of their derivatives.

It is characteristic of compounds containing nitrogen to have a negative constant  $A$  when dissolved in phenol. Hence it is not surprising to find that hippuric and phenylaminophenylacetic acids behave in a similar manner. But, at first sight, it appears anomalous that phenylaminoacetic acid should associate to approximately the same extent as the mono-substituted acids. Thus,

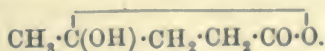
$C_6H_5 \cdot NH \cdot CH_2 \cdot CO_2H$ ,  $A = -17$ ;  $C_6H_5 \cdot NH \cdot CH(C_6H_5) \cdot CO_2H$ ,  $A = -16$ .

This behaviour may be explained if it is remembered that the phenyl group in the  $\alpha$ -position weakens the associating influence of the carboxyl radicle (compare Table I, acids, Nos. 21, 29, 30) and that imino-groups tend to cause negative association.

Aniline has a slight, succinimide a strong negative value of  $A$ . Phenylaminoacetic acid associates; hippuric acid has a negative value of  $A$ , which would appear to be due to the strong negative influence of the  $CO \cdot NH$  group.

### 6. *Acids, the Molecular Depression of which increases with the Concentration.*

Excepting certain substituted amino-acids, the only other compound with a negative constant  $A$  is lævulic acid. Bredt (*Annalen*, 1887, 236, 225) gave the constitution of this acid as



In phenol, lævulic acid behaves as if it contained a hydroxyl group, for the alcohols give negative values for  $A$  as well as a large initial molecular depression (82).

### 7. *Acids with an Ethylenic Linking.*

In benzene solution, the unsaturated alcohols associate more rapidly than the corresponding saturated compounds,\* and, similarly, the value of  $A$  is greater for cinnamic than for phenylpropionic acid. Oleic and stearic acids, on the other hand, show the opposite behaviour (compare Table I).

\* Biltz (*loc. cit.*).



### 8. *Acids which Decompose in the Presence of Phenol.*

Dichloroacetic acid is decomposed by phenol, the solution having a large molecular depression and a characteristic fluorescence, which is red by reflected, and green by transmitted light. Citraconic acid gives a similar fluorescence, probably decomposing into its anhydride, which then condenses with phenol to a compound of the fluorescein type. Maleic acid dissolves to a clear solution.\*

### *The Molecular Depression and the "Rate" of Association.*

No definite connection appears to exist between the initial molecular depression and the constant  $A$  of a compound, although among the fatty acids the two constants generally vary together. The greatest regularity is exhibited by those acids for which  $A$  varies between 13 and 17. In all cases, the molecular depression is 69—71, being almost identical with the mean value of this constant.

Acids with a negative  $A$  (Nos. 34—36, Table I) are shown to have a large initial molecular depression. Experiments on some 20 substances, including alcohols, alkyl esters, and nitrogen compounds, indicate that this is only a particular example of a general rule.

### *The Behaviour of the Fatty Acids.*

If the molecular weights of the fatty acids in benzene solution are plotted against the concentration, the curve rises rapidly until the molecular weight is doubled, and then remains almost constant, even in concentrated solutions. But there is still a slight increase, and the numbers in Table II show its magnitude between a 5 and 10 per cent. concentration. A comparison is made with the corresponding values of  $A$  in phenol.

\* Phenylaminoacetic and phenylaminophenylacetic acids dissolved to yellow solutions, but no fluorescence was observed. In the case of these acids, there was no evidence of decomposition. Diglutaric acid, when dissolved in phenol, yields a dichroic solution.

TABLE II.

| Acid.            | Increase in<br>molecular<br>weight in<br>benzene.* | A. |
|------------------|--|----|
| Acetic.....      | 25   | 23 |
| Propionic .....  | 20   | 13 |
| Phenylacetic ... | 20   | 14 |
| Bromoacetic ...  | 15   | 12 |
| Lauric.....      | 5  | 42 |

TABLE III.

| Acid.              | Etherification<br>constant. | A. |
|--------------------|-----------------------------|----|
| Acetic .....       | 3.661                       | 23 |
| Propionic .....    | 3.049                       | 13 |
| Chloroacetic ...   | 2.432                       | 14 |
| Phenylacetic ...   | 2.068                       | 14 |
| Bromoacetic ...    | 1.994                       | 12 |
| isoButyric .....   | 1.019                       | 9  |
| Trichloroacetic .. | 0.0372                      | 2  |

\* Paternò, *Gazzetta*, 1889, 19, 640.

A rough correspondence is shown in the case of the first four acids, but the difference is considerable for lauric acid. It must, however, be remembered that in benzene solution the acids are present as double molecules.

The rule that substitution in the  $\alpha$ -position with respect to carboxyl diminishes the "rate" of association is by no means confined to the solvent at present under examination. Experiments with thymol show that whilst chloroacetic acid associates rapidly, trichloroacetic acid is practically normal. Again, in phenylacetic acid solution, acetic acid shows a greater increase of association than its monochloro-derivative, and, in the case of trichloroacetic acid, the value of A is actually negative.

Similarly, the normality of trichloroacetic acid in phenol solution finds a parallel in the behaviour of the corresponding tribromo-acid in benzene. For Auwers has shown (*Zeit. physikal. Chem.*, 1890, 8, 689) that this acid has a normal molecular weight with a depression of  $0.2^\circ$ , whilst in a solution of phenylacetic acid causing the same depression there are already 50 per cent. of double molecules.

#### *The Connection between the "Rate" of Association and the Etherification Constant.*

Sudborough and Lloyd (*Trans.*, 1899, 75, 467) have determined the rates of etherification of a number of substituted acetic acids in the presence of hydrochloric acid. The qualitative agreement between their results and the values of A is remarkable. The comparison is shown in Table III.

The numbers in both columns are (with the single exception of propionic acid) in descending order. This relationship strongly supports Henry's theory of esterification, namely, that an unstable additive

product<sub>2</sub> is formed between the alcohol and the acid, and that this immediately decomposes into the alkyl ester. Association, on the other hand, consists of the union of like molecules, but in each case the combination is due to the carboxyl group.

*The Solubility of the Fatty Acids and their Derivatives in Phenol.*

The study of the phenolic solutions of the fatty acids leads to the following generalisations.

(1) The lower fatty acids are miscible in all proportions, but when stearic acid is reached the solubility becomes greatly diminished.

(2) All the hydroxyl, halogen, and phenyl derivatives of the fatty acids are readily soluble.

(3) The polycarboxylic acids are characterised by their insolubility; this also applies to their halogen and hydroxyl derivatives. The solubility, however, is much increased by the introduction of an alkyl group, the effect being smaller the greater the number of carboxyl radicles.

(4) The hydroxyl derivatives of the dibasic acids are less soluble than the original acids.

(5) The  $\alpha$ -amino-acids are extremely insoluble, in this respect differing from their substituted derivatives.

In Table IV, the differences between the freezing points of phenol and its saturated solution are given for a number of slightly soluble acids. This depression is roughly proportional to the number of dissolved molecules in a constant weight of phenol.

TABLE IV.

| Acid.                   | $\Delta t$ .<br>Depression of<br>freezing point<br>of saturated<br>solution. | Acid.                                  | $\Delta t$ .<br>Depression of<br>freezing point<br>of saturated<br>solution. |
|-------------------------|--|--|--|
| 1. Malonic.....         | 0.15°  | 14. Aminoacetic (glycine) ..           | 0.08°  |
| 2. Succinic .....       | 0.22   | 15. $\alpha$ -Aminophenylacetic...     | 0.05   |
| 3. Adipic .....         | 1.3  | 16. Aspartic .....                     | 0.06   |
| 4. Sebacic .....        | 2.1  | 17. Phenylaminoacetic ...              | 1.4  |
| 5. Methylsuccinic ..... | > 3  | 18. Benzoylaminoacetic ...             | 2.1  |
| 6. Ethylmalonic .....   | > 3  | 19. Phenylaminophenyl-<br>acetic ..... | 1.7  |
| 7. Citraconic.....      | > 5  | 20. Palmitic .....                     | 5.2  |
| 8. Mesaconic.....       | 0.27   | 21. Stearic .....                      | 1.6  |
| 9. Maleic .....         | 2.3  | 22. Tricarballic .....                 | 0.17   |
| 10. Fumaric .....       | 0.09   | 23. Aconitic .....                     | 0.35   |
| 11. Bromosuccinic.....  | 0.50   | 24. Diglutaric .....                   | 0.09   |
| 12. Tartaric .....      | 0.09   | 25. <i>iso</i> Propyltricarballic.     | 0.38   |
| 13. Mucic .....         | 0.11   |  |  |



In the series of homologous dibasic acids, Nos. 1—4, it is seen that the solubility increases with the molecular weight. In the case of succinic acid and its methyl derivative, the latter, which is convertible into its anhydride with ease, is considerably more soluble. The introduction of a bromine atom into succinic acid increases the solubility, but to a much smaller extent. Malonic acid dissolves more sparingly than succinic acid, but ethylmalonic acid is easily soluble; isopropyltricarballic acid, however, is only slightly more soluble than tricarballic acid.

Although methylsuccinic acid readily dissolves in phenol, the introduction of a third carboxyl group makes the resulting tricarballic acid almost insoluble. Similarly, aconitic acid is only slightly soluble. Hence it is to be expected that the dibasic acid derived from it would be citraconic acid, as the isomeric mesaconic acid is even less soluble than aconitic acid. From this, it would appear that, when dissolved in phenol, aconitic acid possesses the *cis*-configuration.

Tartaric and mucic acids (Nos. 12 and 13) are considerably less soluble than the acids from which they are derived (2 and 3). This shows clearly the effect of hydroxyl groups in dicarboxylic acids.

The very slight solubility of the  $\alpha$ -amino-acids (Nos. 14, 15, 16) is especially remarkable, but their derivatives (Nos. 17, 18, 19) are more readily soluble.

$\alpha\alpha'$ -Diglutaric acid (No. 24), the only tetrabasic acid examined, illustrates the rule that polycarboxylic acids are extremely insoluble in phenol.

### *Summary and Conclusion.*

The following conclusions have been deduced from the foregoing investigation.

(1) In freezing phenol, the fatty acids and their derivatives tend to associate with an increase of the concentration.

(2) The "rates" of association of the normal fatty acids alternately increases and decreases. If the compounds containing an even number of carbon atoms are considered, the association decreases until a minimum is reached at the sixth member; the subsequent increase is rapid.

(3) The influence of substituents depends on their nature and on their position as well as on the acid into which they are introduced. But it is a general rule that  $\alpha$ -disubstituted acids associate less strongly than the mono-derivatives, whilst trisubstituted acids exhibit the lowest "rate" of association.

(4) Dicarboxylic acids associate more rapidly than monocarboxylic

acids. Here, again, substitution in the  $\alpha$ -position reduces the "rate" of association.

(5)  $\alpha$ -Hydroxy- and isonitroso-groups tend to increase the "rate" of association.

(6) Certain nitrogen groups have a negative influence, that is, the resulting compounds have molecular weights decreasing with the concentration.

(7) The "rate" of association of the substituted acetic acids bears a qualitative relationship to their velocity of etherification (compare V. Meyer, *Ber.*, 1895, 28, 2790).

The present work will be extended in other directions, a number of alcohols, ethereal salts, and hydrocarbons having already been examined in solutions of phenol and its derivatives.

In conclusion, I would like to express my best thanks to Professor Easterfield for the encouragement and help which he has given me during the course of my work. I am also indebted to Professor Auwers of Greifswald, who has furnished me with a considerable amount of literature bearing on cryoscopic investigations.

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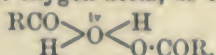
## CXL.—*Acid Salts of Monobasic Acids.*

By ROBERT CROSBIE FARMER, M.Sc., Ph.D.

MANY oxygen compounds, such as cineol, dimethylpyrone, &c., combine with acids to form well-defined salts, which can only be formulated on the assumption that the oxygen has become quadrivalent. Esters have also been shown to possess this property, as, for instance, ethyl benzoate (Baeyer and Villiger, *Ber.*, 1901, 34, 2692). It is therefore evident that one of the oxygen atoms of the carboxyl group can undergo this transformation and impart basic properties to the carboxylic esters. This being the case, it is possible that even the carboxylic acids themselves may also possess extremely feeble basic properties.

It is well known that many carboxylic acids, such as acetic and benzoic acids, give rise to double molecules when dissolved in benzene or other inert solvents, or even in the state of vapour (Beckmann, *Zeit. physikal. Chem.*, 1888, 2, 729; Nernst, *loc. cit.*, 1891, 8, 116; Dawson, *Trans.*, 1902, 81, 521; Hentzschel, *J. pr. Chem.*, 1887, 36,

468). The formation of double molecules may be due to basic properties caused by a quadrivalent oxygen atom, as in the formula



If this be the case, the double compound will be of the nature of a salt, and the assumption is therefore strengthened by the fact that the double molecules only exist in inert solvents such as benzene, chloroform, &c., and are dissociated by hydrolysing solvents. It is probably the hydroxylic oxygen of the carboxyl group which becomes quadrivalent, for if it is assumed that the carbonyl oxygen becomes tetradic, the internal salt,  $\text{RC} \leq \overset{\text{iv}}{\text{O}} \text{H}$ , might be expected.

If this explanation be correct, the tendency to form salts will be increased by the replacement of the acidic hydrogen by a more basic element, such as an alkali metal.

If, however, the above theory is correct, such salts should be capable of entering into combination with the acids from which they are derived. The complex molecules thus formed would then be formulated as follows:  $\begin{array}{c} \text{RCO} > \overset{\text{iv}}{\text{O}} < \text{K} \\ \text{RCO}_2 > \text{O} < \text{H} \end{array}$ .

The existence of double compounds of normal acetates with acetic acid has been long known, and the acid formates have been recently investigated by Groschuff (*Ber.*, 1903, 36, 1783), but in the benzoic acid series only a few isolated examples have been observed, owing to their instability in the presence of water.

The observation that many derivatives of benzoic acid readily give rise to well-defined acid salts led me to study the conditions of formation of these compounds and their stability in solution. A physico-chemical investigation showed that, although they exist to some extent in alcoholic solution, yet in water the dissociation is practically complete. It appears, therefore, that the acid salts, like the complex molecules of the acids, are most easily decomposed by solvents of the water type. The acid salts are, however, more stable in this respect than the associated acids.

Hentzschel (*J. pr. Chem.*, 1887, 36, 468) suggested the formula  $\begin{array}{c} \text{CH}_3 > \text{C} < \text{O} > \text{C} < \text{CH}_3 \\ \text{HO} > & \text{O} & < \text{OH} \end{array}$  for potassium hydrogen acetate. There appears, however, to be no reason why the stability of such a complex should be dependent on the absence of hydrolysing solvents; the assumption that the compound is the salt of an extremely feeble base is, on the other hand, quite in accord with this observation. The formation of acid salts does not therefore necessitate the assumption that the acids are dibasic, but may be supposed to depend on the amphoteric nature of the substance due to the presence of oxygen.



## EXPERIMENTAL.

The potassium and ammonium salts were chosen as typical examples, and their preparation was effected by mixing the theoretical proportions of caustic potash or ammonia and the free acid in alcoholic solution.

In most cases, the acid salts slowly separated, but in some cases the solution remained supersaturated. The salts were purified by recrystallisation from alcohol, and generally the ammonium salts crystallised out more readily than the potassium salts. The para-substituted benzoic acids gave rise to the most sparingly soluble acid salts, whilst those of the ortho- and meta-compounds could in some cases be obtained only by concentrating the solution to a very small bulk. The salts are at once decomposed in water, and the free acid can therefore be estimated by titration.

Potassium hydrogen benzoate, which was found by Gerhardt (*Jahresber.*, 1852, 450) in the residue left after distilling potassium acetate with benzoyl chloride, is more easily obtained pure by the foregoing method. It is sparingly soluble in alcohol and separates in colourless, leafy crystals.

Analysis: The percentage values of potassium and free benzoic acid were  $K = 13.85$ ;  $C_6H_5 \cdot CO_2H = 43.02, 43.22, 43.19$ , the calculated values being  $K = 13.86$ ;  $C_6H_5 \cdot CO_2H = 43.25$ .

*Ammonium hydrogen benzoate*, obtained in a similar manner, crystallised from alcohol in colourless plates.

Found,  $NH_4 = 7.1$ ;  $(C_6H_5 \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 6.9$  per cent.

The salt is sparingly soluble in alcohol, insoluble in ether and chloroform, and melts indefinitely at  $190^\circ$ , subsequently yielding a sublimate; it does not, therefore, appear to be identical with the isomeric dibenzamide hydrate,  $(C_6H_5 \cdot CO)_2NH \cdot 2H_2O$ , obtained by Schäfer (*Annalen*, 1873, 169, 111), as the latter compound was soluble in the above solvents and melted at  $99^\circ$  (compare Beilstein's *Handbuch*, 3rd edition, 1896, vol. ii, p. 1171).

Ethyl benzoate has been previously found by Baeyer and Villiger to yield salts containing quadrivalent oxygen (*Ber.*, 1901, 34, 2692). An attempt was made to prepare a double compound of ethyl benzoate with benzoic acid, but no combination took place, either in benzene solution or on crystallising benzoic acid from ethyl benzoate.

*Toluic Acids.*—*p*-Toluic acid readily gave rise to acid salts, whilst those of *m*-toluic acid only separated with difficulty from their alcoholic solutions. *o*-Toluic acid did not under these conditions give acid salts; on concentrating the solution to a very small bulk, the free toluic acid separated, together with a small quantity of the normal salt.

*Potassium hydrogen m-toluate* is very readily soluble in alcohol and crystallises in long needles.

Found,  $K = 12.87, 12.66$ ; free toluic acid  $= 43.6$ ;  
 $(CH_3 \cdot C_6H_4 \cdot CO_2)_2HK$  requires  $K = 12.61$ ;  $CH_3 \cdot C_6H_4 \cdot CO_2H = 43.9$   
 per cent.

*Ammonium hydrogen m-toluate* forms tabular crystals moderately soluble in alcohol.

Found,  $NH_4 = 6.2$ ;  $(CH_3 \cdot C_6H_4 \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 6.2$  per cent.

*Potassium hydrogen p-toluate* forms beautiful, large laminæ, sparingly soluble in alcohol.

Found,  $K = 12.31$ ;  $(CH_3 \cdot C_6H_4 \cdot CO_2)_2HK$  requires  $K = 12.61$  per cent.

*Ammonium hydrogen p-toluate* forms long needles sparingly soluble in alcohol.

Found,  $NH_4 = 6.1$ ;  $(CH_3 \cdot C_6H_4 \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 6.2$  per cent.

*Bromobenzoic acids.* Here, again, the acid salts of the *p*-derivative are the most sparingly soluble. The solutions of the ortho-derivatives tend to become greatly supersaturated.

*Potassium hydrogen o-bromobenzoate* forms needle-shaped crystals very readily soluble in alcohol.

Found,  $K = 8.94$ ; free *o*-bromobenzoic acid  $= 46.0$ ;  
 $(C_6H_4Br \cdot CO_2)_2HK$  requires  $K = 8.89$ ;  $C_6H_4Br \cdot CO_2H = 45.7$  per cent.

*Ammonium hydrogen o-bromobenzoate* is likewise very soluble in alcohol and forms flat, prismatic crystals.

Found,  $NH_4 = 4.5$ ;  $(C_6H_4Br \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 4.3$  per cent.

*Potassium hydrogen m-bromobenzoate* forms colourless plates readily soluble in alcohol.

Found,  $K = 8.69$ ; free *m*-bromobenzoic acid  $= 46.1$ ;  
 $(C_6H_4Br \cdot CO_2)_2HK$  requires  $K = 8.89$ ;  $C_6H_4Br \cdot CO_2H = 45.7$  per cent.

*Ammonium hydrogen m-bromobenzoate*, colourless plates.

Found,  $NH_4 = 4.4$ ;  $(C_6H_4Br \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 4.3$  per cent.

*Potassium hydrogen p-bromobenzoate*, colourless leaflets, very sparingly soluble in cold alcohol.

Found,  $K = 8.78$ ;  $(C_6H_4Br \cdot CO_2)_2HK$  requires  $K = 8.89$  per cent.

*Ammonium hydrogen p-bromobenzoate* crystallises in large laminæ.

Found,  $\text{NH}_4 = 4.3$ ;  $(\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2)_2\text{H}\cdot\text{NH}_4$  requires  $\text{NH}_4 = 4.3$  per cent.

*Nitrobenzoic Acids.*—The acid salts derived from these are for the most part sparingly soluble in alcohol.

*Potassium hydrogen o-nitrobenzoate* forms large, pale yellow, flat prisms.

Found,  $\text{K} = 10.60$ ; free *o*-nitrobenzoic acid  $= 45.1$ ;  
 $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{HK}$  requires  $\text{K} = 10.51$ ;  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} = 44.9$  per cent.

With alcoholic ammonia, *o*-nitrobenzoic acid yielded only the normal ammonium salt.

*Potassium hydrogen m-nitrobenzoate* forms small, pale yellow needles.  
 Found,  $\text{K} = 10.43$ ; free *m*-nitrobenzoic acid  $= 45.0$ ;  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{HK}$  requires  $\text{K} = 10.51$ ;  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} = 44.9$  per cent.

Ammonium hydrogen *m*-nitrobenzoate has been described by Mulder (*Annalen*, 1840, 34, 304); it forms pale yellow needles.

Found,  $\text{NH}_4 = 4.9$ ;  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{H}\cdot\text{NH}_4$  requires  $\text{NH}_4 = 5.1$  per cent.

*Potassium hydrogen p-nitrobenzoate* forms pale yellow needles, sparingly soluble in alcohol.

Found,  $\text{K} = 10.26$ ;  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{HK}$  requires  $\text{K} = 10.51$  per cent.

*Ammonium hydrogen p-nitrobenzoate*, small, pale yellow needles.

Found,  $\text{NH}_4 = 4.9$ ;  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{H}\cdot\text{NH}_4$  requires  $\text{NH}_4 = 5.1$  per cent.

*Hydroxybenzoic Acids.*—Several acid salts of salicylic acid are already known (Hoffmann, *Jahresber.*, 1878, 759); they slowly separated from saturated aqueous solutions of salicylic acid and neutral salicylates, but are more easily prepared by the method described on p. 1442.

*Potassium hydrogen salicylate*, small prisms, moderately soluble in alcohol.

Found, free salicylic acid, 44.1;  $(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{HK}$  requires  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} = 43.9$  per cent.

The acid salt of *m*-hydroxybenzoic acid could not be obtained free from the normal salt, since the alcoholic solution remained persistently supersaturated. The product obtained on repeated crystallisation was acid, but still contained some of the normal salt, as shown by acidi-



metry and potassium determinations. No free *m*-hydroxybenzoic acid could be extracted by benzene; hence an acid salt must have been present in the mixture.

*Potassium hydrogen p-hydroxybenzoate* is sparingly soluble in alcohol and crystallises in laminæ.

Found,  $K = 12.63$ ;  $(HO \cdot C_6H_4 \cdot CO_2)_2HK$  requires  $K = 12.45$  per cent.

*Ammonium hydrogen p-hydroxybenzoate* forms small prisms sparingly soluble in cold alcohol.

Found,  $NH_4 = 5.9$ ;  $(HO \cdot C_6H_4 \cdot CO_2)_2H \cdot NH_4$  requires  $NH_4 = 6.1$  per cent.

The foregoing results show that the capacity to form salts containing two equivalents of acid to one of potassium or ammonium is a general property of the derivatives of benzoic acid. In the solid state, these derivatives are well-defined compounds, exhibiting in most cases, beautiful crystalline forms, and recrystallising unchanged from alcohol. Benzene has no solvent action on them, thus indicating the absence of any uncombined acid. On heating, they undergo no change at the melting points of the corresponding acids, but only break up at much higher temperatures, yielding a sublimate of the acid or its decomposition products. These acid salts have therefore many properties quite distinct from those of mixtures of the normal salts with the free acids.

*Effect of Water and Alcohol on the Acid Salts.*—The acid salts are at once decomposed in contact with water. The following method was adopted in order to ascertain whether this dissociation is complete in aqueous solution.

A weighed quantity of benzoic acid was distributed between known volumes of water and benzene at a constant temperature ( $25^\circ$ ). Since the ratio of distribution alters with the dilution (Nernst, *Zeit. physikal. Chem.*, 1891, 8, 112), the same concentration was maintained throughout. The experiment was now repeated, using a solution of potassium benzoate in place of pure water. If the potassium benzoate combined with any appreciable quantity of the free benzoic acid to form the compound  $(C_6H_5CO_2)_2HK$ , the ratio of distribution of the benzoic acid between the two solvents would be affected.

A correction must, of course, be made for the ionisation of the benzoic acid. In the following tables, the ratio of distribution has been expressed in terms of non-ionised benzoic acid. The experiments were carried out with 60 c.c. of benzene and 500 c.c. of water free from carbonic acid.

*Distribution of Benzoic Acid between Benzene and Water.*

Temperature = 25°.

| Gram-mol. of benzoic acid per litre of water. | Gram-mol. of non-ionised benzoic acid per litre of water. | Gram-mol. of benzoic acid per litre of benzene. | Ratio of distribution of non-ionised benzoic acid between benzene and water. |
|---|---|---|--|
| 0·01640                                       | 0·01545   | 0·2732  | 17·7   |
| 0·01645                                       | 0·01550   | 0·2727  | 17·6   |
| 0·01655                                       | 0·01559   | 0·2719  | 17·4   |
|   |   |   | <hr/> Mean 17·6  |

*Distribution of Benzoic Acid between Benzene and an Aqueous Solution of Potassium Benzoate.*

Temperature = 25°.

| Gram-mol. of potassium benzoate per litre of water. | Gram-mol. of benzoic acid per litre of water. | Gram-mol. of benzoic acid per litre of benzene. | Ratio of distribution of benzoic acid between benzene and the aqueous solution. |
|---|---|---|---|
| 0·0093  | 0·01587                                       | 0·2776  | 17·5  |
| 0·028   | 0·01597                                       | 0·2768  | 17·3  |
| 0·047   | 0·01603                                       | 0·2762  | 17·2  |
|   |   |   | <hr/> Mean 17·3   |

The addition of potassium benzoate to the extent of nearly three gram-molecules for each gram-molecule of benzoic acid in the aqueous layer has therefore scarcely affected the ratio of distribution of the acid, and hence the amount of the double compound present in aqueous solution must be very small.

Experiments on the distribution of acetic acid between chloroform and an aqueous solution of sodium acetate have been made by Dawson and Grant (*Trans.*, 1902, 81, 512). Higher concentrations must be employed than with benzoic acid on account of the low coefficient of distribution. The following experiments were carried out with benzene, and, as before, the same concentration was maintained throughout.

*Distribution of Acetic Acid between Benzene and Water.*

Temperature = 25°.

| Gram-mol. of acetic acid per litre of water. | Gram-mol. of non-ionised acetic acid per litre of water. | Gram-mol. of acetic acid per litre of benzene. | Ratio of distribution of non-ionised acetic acid between benzene and water. |
|--|--|--|---|
| 0.868  | 0.864  | 0.0244   | 0.0282  |
| 0.865  | 0.861  | 0.0243   | 0.0282  |
|  |  |  | Mean 0.0282   |

*Distribution of Acetic Acid between Benzene and an Aqueous Solution of Sodium Acetate.*

Temperature = 25°.

| Gram-mol. of sodium acetate per litre of water. | Gram-mol. of acetic acid per litre of water. | Gram-mol. of acetic acid per litre of benzene. | Ratio of distribution of acetic acid between benzene and the aqueous solution. |
|---|--|--|--|
| 0.13  | 0.867  | 0.0249   | 0.0287   |
| 0.25  | 0.869  | 0.0246   | 0.0284   |
| 0.38  | 0.872  | 0.0250   | 0.0287   |
| 0.50  | 0.866  | 0.0250   | 0.0289   |
|   |  |  | Mean 0.0287  |

The sodium acetate has therefore slightly decreased the solubility of the acetic acid in the water. In view of the unavoidably high concentrations, this is not surprising; Dawson and Grant found that tartaric acid exerted a similar influence (Trans., 1902, 81, 512). There is therefore no evidence for the existence of acid acetates or benzoates in aqueous solution. It appears, however, probable that the complex molecules will exist to some extent in the presence of a large excess of the normal salt, for it was found that when a small quantity of mineral acid was added to a concentrated solution of potassium benzoate, the precipitate formed was not pure benzoic acid, but consisted of the foregoing potassium hydrogen salt.

As already mentioned, the double salts can be crystallised from alcohol without change. Molecular weight determinations were carried out by the ebullioscopic method to ascertain whether dissociation took place on dissolving the salt. The potassium hydrogen *p*-hydroxybenzoate was chosen for these determinations.



*Molecular Weight of Potassium Hydrogen p-Hydroxybenzoate in Alcoholic Solution.*

A mixture of  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{K}$  requires 157.  
 $(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{HK}$  „ 314.

| Solvent. | Substance. | Rise of<br>boiling point.<br>$\Delta t.$ | Molecular<br>weight. |
|----------|------------|--|----------------------|
| 23.75    | 0.625      | 0.185                                    | 164                  |
| 23.75    | 1.807      | 0.503                                    | 174                  |

The molecular weight found is therefore somewhat higher than that calculated for complete dissociation. We should expect a mixture of a salt and an acid to give a value somewhat lower than that calculated owing to ionic dissociation in the alcohol (compare Jones, *Zeit. physikal. Chem.*, 1899, 31, 133), but the result points to a partial association.

This was confirmed by the following more decisive method. In this case, the corresponding salt of salicylic acid was employed, the molecular weight of normal potassium salicylate being first determined.

*Molecular Weight of Normal Potassium Salicylate in Alcoholic Solution.*

Molecular weight of  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{K} = 176$ .

| Solvent. | Substance. | Rise of<br>boiling point.<br>$\Delta t.$ | Molecular<br>weight. |
|----------|------------|--|----------------------|
| 23.75    | 0.639      | 0.187                                    | 165                  |
| 23.75    | 1.119      | 0.328                                    | 165                  |

As was to be expected, the molecular weight found is somewhat lower than that calculated, owing to ionisation. Salicylic acid was now added to the alcohol, already containing the normal salicylate, and the further rise of boiling point observed.

If there were no combination between the acid and its normal salt, the simple molecular weight should be obtained for the salicylic acid added. If, however, any acid salt is formed, a higher molecular weight will be found; this should be especially noticeable at first, when there is very little salicylic acid, and, consequently, a large excess of the normal salt.

*Molecular Weight of Salicylic Acid in Alcohol containing  
4.72 per cent. of Normal Potassium Salicylate.*

Molecular weight of  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} = 138$ .

| Solvent. | Substance. | Rise of<br>boiling point.<br>$\Delta t$ . | Molecular<br>weight. |
|----------|------------|---|----------------------|
| 23.75    | 0.1805     | 0.046                                     | 190                  |
| "        | 0.388      | 0.112                                     | 168                  |
| "        | 0.642      | 0.199                                     | 156                  |
| "        | 1.091      | 0.364                                     | 145                  |
| "        | 1.455      | 0.481                                     | 146                  |

As was anticipated, the observed molecular weight was much higher than the normal value in presence of a large excess of the normal salt, but fell gradually as the quantity of salicylic acid increased. It is evident, therefore, that even in alcoholic solution the complex salt is for the most part dissociated into the free acid and the normal salt.

THE UNIVERSITY,  
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## CXLI.—*The Constitution of Certain Silicates.*

By CHARLES SIMMONDS, B.Sc.

DURING the course of some investigations on the properties of lead silicates, it was noticed that oxygen was readily removed from these compounds when they were heated in a current of hydrogen.

In a qualitative sense, this phenomenon is not unfamiliar, the blackening of lead glass in the reducing flame of the blowpipe being perhaps the best known instance. Hitherto, however, no quantitative study of the reaction appears to have been recorded. In the present experiments, it has been found that the weight of oxygen which can be eliminated from a lead silicate by the action of hydrogen at a red heat corresponds exactly, within the limits of experimental error, to the quantity of lead present. For each atom of lead contained in the silicate, one atom of oxygen, and only one, is removed from the silicate by the reducing agent.

The following table embodies the quantitative results yielded by a number of lead silicates:

TABLE A.  
*Reduction of Lead Silicates.*

0.5 gram of silicate heated to redness in a current of hydrogen.

| Silicate.  | Percentage of lead in silicate calculated as PbO. | Oxygen corresponding with weight of PbO present. | Oxygen eliminated.            |                             |
|--|---|--|-------------------------------|-----------------------------|
|  |   |  | Deducted from loss of weight. | Deducted from water formed. |
| I. <i>Simple silicates</i> :—  |   | Gram.  | Gram.                         | Gram.                       |
| Lead orthosilicate, $\text{Pb}_2\text{SiO}_4$ .....  | 88.1  | 0.032  | 0.033                         | 0.032                       |
| „ metasilicate, $\text{PbSiO}_3$ .....   | 78.7  | 0.028  | 0.027                         | 0.029                       |
| „ polysilicate, $\text{Pb}_2\text{Si}_3\text{O}_8$ .....   | 71.1  | 0.025  | 0.024                         | 0.025                       |
| „ disilicate, $\text{PbSi}_2\text{O}_5$ .....  | 64.9  | 0.023  | 0.022                         | 0.023                       |
| II. <i>Double or complex silicates</i> :—  |   |  |                               |                             |
| Silicates of lead, aluminium, and the alkali and alkaline earth metals, assignable to the following classes :— |   |  |                               |                             |
| <i>Metasilicates</i> :—No. 1 .....   | 59.3  | 0.021  | 0.021                         | 0.022                       |
| „ 2 .....  | 46.8  | 0.017  | 0.018                         | 0.017                       |
| „ 3 .....  | 48.7  | 0.018  | 0.018                         | —*                          |
| „ 4 .....  | 70.4  | 0.025  | 0.024                         | 0.023                       |
| „ 5 .....  | 70.3  | 0.025  | 0.025                         | —*                          |
| <i>Polysilicates</i> :— „ 6 .....  | 24.5  | 0.009  | 0.009                         | 0.009                       |
| „ 7 .....  | 41.3  | 0.015  | 0.013                         | 0.014                       |
| „ 8 .....  | 41.4  | 0.015  | 0.015                         | 0.014                       |
| „ 9 .....  | 49.3  | 0.018  | 0.017                         | 0.018                       |
| „ 10 .....   | 53.2  | 0.019  | 0.019                         | 0.017                       |
| <i>Disilicates</i> :— „ 11 .....   | 44.1  | 0.016  | 0.018                         | —*                          |
| (Flint glass) „ 12 .....   | 44.6  | 0.016  | 0.018                         | 0.017                       |

\* Water not determined.

The hydrogen used in the experiments was freed from oxygen, moisture, hydrogen arsenide, and hydrogen sulphide by being passed successively through or over (1) an alkaline solution of lead nitrate; (2) sulphuric acid; (3) palladium-asbestos; (4) sulphuric acid; (5) red-hot copper turnings; and (6) sulphuric acid. The finely powdered silicate, dried at  $100^\circ$ , was weighed into a porcelain boat, placed in a tube of hard glass, and heated in a combustion furnace for an hour or more in a current of hydrogen. The water produced was absorbed in a small U-tube containing sulphuric acid and pumice. After being allowed to cool in a stream of dry hydrogen, the boat with its residue was weighed, as was also the U-tube.



Since some of the silicates investigated contained water of constitution, and others were notably hygroscopic, a second portion of the substance, weighed out at the same time, was heated to redness in air and its loss of weight determined. Due allowance for this loss was then made in the reduction experiments.

As a rule, the differences shown between the two methods of estimation are mainly due to experimental errors arising from hygroscopicity. Small inaccuracies may also occasionally arise from the presence of a small amount of pyrites or other impurity in the silicates under treatment. Errors due to the first-named cause could be minimised by using a somewhat more complicated form of apparatus; but in the present connection, none of the sources of inaccuracy mentioned is of any particular significance.

In many cases, the reaction commences at a temperature below that of visible red heat. For its completion, however, a bright red heat is usually required. The reduced lead silicate thus obtained is a black powder which does not readily reoxidise. Apparently it does not, as a rule, contain metallic lead. To this, however, there is an exception in the case of lead orthosilicate, which yields a residue containing a considerable quantity of the metal. Further description of the properties of these reduced silicates is deferred until another occasion, since it is a matter distinct from the main object of the present communication.

With certain exceptions, silicates of metals other than lead behave in a similar manner to the lead silicates, provided that the metal (for example, copper, iron, cobalt, nickel, &c.) is one the oxide of which is reducible at a red heat. But the silicates of metals (for example, aluminium, zinc, magnesium, calcium, and the alkali metals), the oxides of which are not thus reducible, do not yield their oxygen at any temperature below that at which the glass of a combustion tube softens. Direct experiments on the silicates in question prove this point, and it is also illustrated by the results for the complex silicates given in the foregoing table. Here the several specimens, which contain from 3 to 23 per cent. of the oxides of aluminium, calcium, magnesium, sodium, and potassium, in addition to the lead oxide, give up oxygen corresponding with the lead only.

The naturally occurring silicates, augite, epidote, and staurolite, are the only exceptions hitherto encountered. These minerals contained from 5 to 15 per cent. of iron oxide, but gave no definite evidence of reduction when heated for an hour in hydrogen. Specimens of hypersthene, ilvaite, and stilpnomelane showed only partial reduction when similarly treated. Such instances may prove to be of importance as indicating something of the differences of constitution which exist in silicates. For the present, however, the discussion is confined to those cases in which the reduction is complete, in the sense already indicated.

In the following tables are given the results obtained with various silicates of copper, iron, cobalt, and nickel:

TABLE B.

*Silicates containing Reducible Oxides other than Lead Oxide.*

0.5 gram of silicate heated to redness in a current of hydrogen.

| Silicate.   | Percentage of reducible oxide in silicate.   | Oxygen corresponding with the reducible oxide. | Oxygen eliminated.            |                             |
|---|--|--|-------------------------------|-----------------------------|
|   |  |  | Deducted from loss of weight. | Deducted from water formed. |
| I. <i>Complex boro-silicates</i> , of the general type $5\text{RO}, \text{Al}_2\text{O}_3, 15 \left\{ \begin{array}{l} \text{SiO}_2 \\ \text{B}_2\text{O}_3 \end{array} \right. :-$ |  |  |                               |                             |
| (a) Lead and copper .....   | PbO = 17.5<br>CuO = 8.1                      | } 0.014  | Gram. 0.015                   | Gram. 0.014                 |
| (b) ,, iron.....  | PbO = 25.9<br>$\text{Fe}_2\text{O}_3 = 14.9$ |  |                               |                             |
| (c) ,, cobalt .....   | PbO = 24.2<br>CoO = 15.6                     | } 0.025  | 0.024                         | 0.024                       |
| (d) ,, nickel.....  | PbO = 25.7<br>NiO = 8.2                      |  |                               |                             |
| The above are commercial silicates prepared by fusion methods.  |  |  |                               |                             |
| II. <i>Double silicates</i> :—  |  |  |                               |                             |
| (a) Copper and sodium .....   | CuO = 38.4                                   | 0.039  | 0.037                         | 0.040                       |
| (b) Iron ,, .....   | $\text{Fe}_2\text{O}_3 = 26.4$               | 0.040  | 0.041                         | 0.041                       |
| (c) Cobalt ,, .....   | CoO = 24.3                                   | 0.025  | 0.023                         | 0.023                       |
| (d) Nickel ,, .....   | NiO = 38.5                                   | 0.041  | 0.042                         | 0.042                       |
| These are silicates obtained by precipitation.  |  |  |                               |                             |

In all the foregoing cases, the figures show that the reduction in question has been complete, or practically so. With the natural silicates, however, this is not the case, and as regards their deportment towards hydrogen, they may be divided into two or three distinct classes of compounds. Although the greater number of the natural silicates so far examined exhibit complete reduction under the conditions of the experiment described, yet in a few cases the reaction is only partial, and in others there is no certain evidence of any reduction whatever,

TABLE C.

*Various Natural Silicates containing Reducible Oxides.*

0.5 gram of silicate heated to redness in a current of hydrogen.

| Silicate.  | Percentage of reducible oxide in silicate. | Oxygen corresponding with the reducible oxide. | Oxygen eliminated.            |                             |
|--|--|--|-------------------------------|-----------------------------|
|  |  |  | Deducted from loss of weight. | Deducted from water formed. |
| (a) <i>Completely reduced, or practically so:—</i> |  |  |                               |                             |
| (1) Diopase .....                                  | CuO = 50.0                                 | Gram. 0.050                                    | Gram. 0.047                   | Gram. 0.050                 |
| (2) Chrysocolla .....                              | CuO = 45.0                                 | } 0.050  | 0.046                         | 0.049                       |
|  | Fe <sub>2</sub> O <sub>3</sub> = 3.5       |  |                               |                             |
| (3) Garnierite .....                               | NiO = 29.6                                 | 0.032  | 0.033                         | 0.036                       |
| (4) Connarite.....                                 | NiO = 23.8                                 | } 0.029  | 0.030                         | —                           |
|  | Fe <sub>2</sub> O <sub>3</sub> = 2.4       |  |                               |                             |
| (5) Chloropal.....                                 | Fe <sub>2</sub> O <sub>3</sub> = 16.4      | 0.025  | 0.024                         | 0.027                       |
| (6) Glauconite .....                               | Fe <sub>2</sub> O <sub>3</sub> = 13.9      | } 0.023  | 0.021                         | —                           |
|  | FeO = 2.5                                  |  |                               |                             |
| (7) Cronstedtite.....                              | Fe <sub>2</sub> O <sub>3</sub> = 55.2      | } 0.105  | 0.106                         | 0.107                       |
|  | FeO = 20.4                                 |  |                               |                             |
| (8) Thuringite .....                               | FeO* = 46.4                                | 0.051  | 0.048                         | 0.048                       |
| (b) <i>Partially reduced:—</i>                     |  |  |                               |                             |
| (1) Ilvaite .....                                  | Fe <sub>2</sub> O <sub>3</sub> = 12.5      | } 0.064  | 0.053                         | 0.057                       |
|  | FeO = 41.2                                 |  |                               |                             |
| (2) Stilpnomelane.....                             | FeO* = 31.2                                | 0.035  | 0.028                         | 0.025                       |
| (3) Hypersthene .....                              | FeO* = 17.6                                | 0.020  | 0.005                         | 0.006                       |
| (c) <i>Not showing definite reduction:—</i>        |  |  |                               |                             |
| (1) Staurolite.....                                | FeO* = 10.2                                | 0.011  | —                             | —                           |
| (2) Augite .....                                   | Fe <sub>2</sub> O <sub>3</sub> = 5.2       | 0.008  | —                             | —                           |
| (3) Epidote .....                                  | Fe <sub>2</sub> O <sub>3</sub> = 14.8      | 0.022  | —                             | —                           |

\* Total iron calculated as FeO. A little Fe<sub>2</sub>O<sub>3</sub> was present.

In the experiments with augite and epidote, the loss of weight, which might have been due to reduction, was less than a milligram. The staurolite specimen showed a somewhat greater loss, but the residue after treatment did not differ perceptibly from the original powder.

From the foregoing experiments, it is obvious that a part of the oxygen in the silicate differs fundamentally from the remainder, and it seems certain that this portion is directly connected with the metal. For instance, one atom of oxygen is removed from the silicate PbSiO<sub>3</sub> by the method indicated, whilst 2, 6, and 17 atoms are



withdrawn from the compounds  $\text{Pb}_2\text{Si}_3\text{O}_7$ ,  $\text{Na}_6\text{Pb}_6\text{Si}_{22}\text{O}_{33}$ , and  $\text{H}_{40}\text{Na}_6\text{Cu}_{17}\text{Si}_{27}\text{O}_{94}$  respectively. The conclusion appears inevitable that the oxygen removed was directly connected in the silicate with the metal which forms a reducible oxide.

No doubt it is *a priori* probable that the metal in any silicate is attached to oxygen in the silicate molecule. But the foregoing observation seems worthy of being recorded, because it removes the matter from the region of probability to that of experimental demonstration—at least so far as the compounds under examination are concerned.

As regards those metals which do not form oxides reducible under the given conditions, the evidence bearing on the mode of attachment of the metal in the silicate is naturally less direct. A few considerations may, however, be adduced which tend to show that any deductions drawn from the behaviour of the silicates of lead, copper, iron, &c., will probably apply to the silicates of the other metals also, in so far as the arrangement of the atoms in the silicate molecule is concerned.

If it were practicable to choose such a temperature and reducing agent as would avoid the simultaneous production of silicide, a silicate like calcium metasilicate,  $\text{CaSiO}_3$ , would no doubt be reduced to  $\text{CaSiO}_2$  precisely as is the case with the corresponding lead and copper compounds. The arguments deduced from these latter compounds would then apply equally to the calcium silicate.

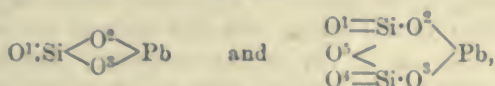
In many crystalline silicates, metals forming oxides of the same type replace one another isomorphously. Alumina, for instance, replaces ferric oxide in tourmaline, garnet, augite, &c., and magnesium oxide is interchangeable with ferrous oxide in the group of ferromagnesian silicates. Hence the interchangeable metals most probably occupy the same positions in the silicate molecule. Consequently, any conclusion regarding structure drawn from the behaviour of the iron oxides in these silicates may, in default of evidence to the contrary, be presumed to hold for the aluminium and magnesium oxides which replace the oxides of iron.

On the whole, therefore, although the evidence does not amount to definite proof, it tends to show that, as regards the mode of attachment, there is no fundamental difference between the metals which form easily reducible oxides and those which do not.

A first approximation to a structural formulation of the silicates in question may now be made. In the case of the silicates of lead, copper, cobalt, &c., it is certainly justifiable to express the relation between removable oxygen and metal by writing the formula as an aggregate of molecular groups, for example,  $2\text{PbO}, 3\text{SiO}_2$ , rather than

in the "salt" form,  $\text{Pb}_2\text{Si}_3\text{O}_8$ . In the case of the other silicates, it is, for the reasons given, at least probable that the same relationship holds. Consequently one would, for instance, be justified in writing  $\text{PbO}, \text{CaO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$  instead of  $\text{PbCaAl}_2\text{Si}_6\text{O}_{18}$ , and this not merely on the ground of orderly arrangement, but as an expression of the fact that the groups exist as such within the silicate molecule.

The ordinary formulæ for the two simple lead silicates  $\text{PbSiO}_3$  (metasilicate) and  $\text{PbSi}_2\text{O}_5$  (metadisilicate) are :



the oxygen atoms being numbered for convenience of reference.

Then the removable oxygen atom is not one of those marked  $\text{O}^1$ ,  $\text{O}^4$  or  $\text{O}^5$ , because (i) it has already been shown that the mobile oxygen must be attached to the lead, and (ii) if it were  $\text{O}^1$ ,  $\text{O}^4$  or  $\text{O}^5$ , there is no reason, since these are not connected with the metal, why an oxygen atom should not be removed when calcium or magnesium is present instead of lead.

The removable oxygen atom is therefore either  $\text{O}^2$  or  $\text{O}^3$ . But these are similarly situated in the formulæ, and should therefore be removed by hydrogen with equal facility. These formulæ, therefore, do not satisfactorily explain the removal of only one atom of oxygen when the silicates are reduced by hydrogen.

There are, in fact, two conditions which an acceptable formula must satisfy :

(i) It must show at least one atom of oxygen (the removable one) attached to each atom of lead.

(ii) It must show that this atom of oxygen differs in some way from any other atom of oxygen that may be attached to the same atom of lead.

A further condition may be mentioned as desirable on general grounds, although it is not strictly required in the case of the simple lead silicates taken as examples. The formula should, as far as possible, be of general applicability as regards its fundamental structure, and particularly in regard to the occurrence of univalent metals in the complex silicates. This last point is of some importance in the study of silicate structure, because a univalent metal, of course, cannot act as a connecting medium between two parts of the silicate molecule.

*Application to the Simpler Lead Silicates. The Metasilicate,  $\text{PbSiO}_3$ .—*To satisfy condition (i), the formula should be written as  $\text{PbO}\cdot\text{SiO}_2$ , or



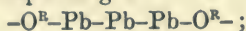
more generally as  $(\text{PbO}:\text{SiO}_2)_n$ , since the molecular weight is not known.

As regards condition (ii), the removable oxygen atom, now indicated as  $\text{O}^{\text{R}}$ , must be considered. Since the molecule contains only atoms of oxygen, silicon, and lead, it follows that  $\text{O}^{\text{R}}$ , besides being attached to its own lead atom, must either be connected with another lead atom, or with silicon, or with another oxygen atom.

But  $\text{O}^{\text{R}}$  cannot be connected with a second lead atom, for there is no way of arranging the group  $\text{Pb}''_n\text{O}_n$  so that all the oxygen valencies shall be satisfied by lead atoms, and still allow of the complex being connected to the rest of the silicate molecule. Nor is it probable that the atom  $\text{O}^{\text{R}}$  is attached to silicon, since oxygen so combined is not very easily removed by hydrogen. If it be urged that such a removal might take place by reason of the influence of the lead atom, this is equally an argument against the usually accepted formula, for there is then no reason why *both* the oxygen atoms attached to lead should not be removed from the compound  $\text{O}:\text{Si} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Pb}$ .

Hence, most probably,  $\text{O}^{\text{R}}$  is attached to another oxygen atom.

The lead atom attached to  $\text{O}^{\text{R}}$  is not likely to be connected with another lead atom, because this is only possible in the special case where there are two lead atoms in the silicate molecule, or an even number arranged in groups of two. Where there are three or more lead atoms connected with one another, only the end atoms can be attached also to the corresponding  $\text{O}^{\text{R}}:^1$



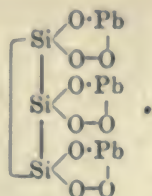
whereas it has already been shown that each atom of lead must be attached to an atom of oxygen.

Moreover, it may be urged against this type of structure that it excludes univalent metals altogether, and is, therefore, not of general applicability. Nor does it seem probable that the lead atom is directly attached to silicon. The silicate is produced by the fusion of lead monoxide and silica, and this—considering the known affinity of silicon for oxygen—appears to preclude altogether any likelihood of the lead and silicon atoms being in direct connection. Indeed, no formulations of silicates are ever made in which the metal is indicated as being directly attached to the silicon atom.

Hence the most probable conclusion appears to be that the lead atom, as well as the  $\text{O}^{\text{R}}$  atom, is attached to a second oxygen atom.

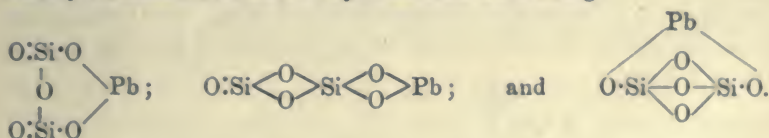
But, if this be so, the only way of writing  $(\text{PbO}:\text{SiO}_2)_n$  to express the fact is  $(>\text{Si} \begin{smallmatrix} \text{O} \cdot \text{Pb} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{O} \end{smallmatrix})_n$ . Taking  $n$  for convenience as equal to 3, the structural formula of lead metasilicate would then be as follows:



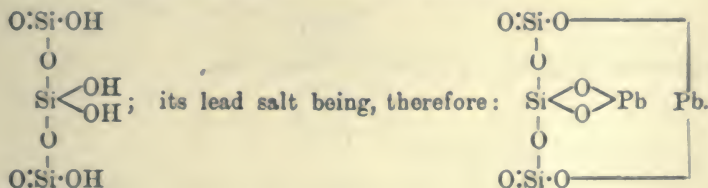


It should be noted that whilst this formula satisfies condition (ii) (p. 1455), this condition has not been used in establishing the formula.

*Disilicates and Trisilicates.*—The hypothetical acid,  $\text{H}_2\text{Si}_2\text{O}_5$ , corresponding with the second anhydride of disilicic acid,  $\text{H}_6\text{Si}_2\text{O}_7$ , is usually formulated in three ways, the lead salts being:



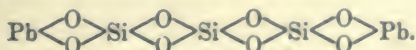
As regards the trisilicates, the hypothetical acid,  $\text{H}_4\text{Si}_3\text{O}_8$ , is usually formulated as the second anhydride of ortho-trisilicic acid:



Erdmann (*Lehrbuch der Anorganischen Chemie*, p. 489), formulates the acid thus:

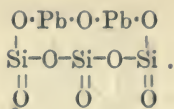


the corresponding lead silicate being, therefore:



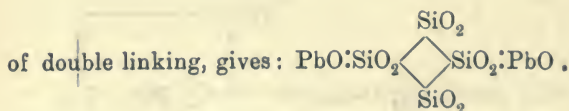
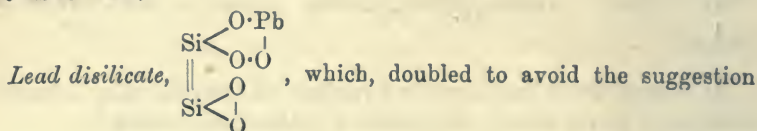
Silicates of this class are also formulated as a combination of one molecule of a metasilicate with one of a disilicate. Thus, Groth formulates orthoclase as  $\text{O} \cdot \text{Si} \begin{array}{c} \diagup \text{O} \diagdown \\ | \text{O} | \end{array} \text{Al} \cdot \text{O} \cdot \text{Si} \cdot \text{O} \cdot \text{Si} \cdot \text{O} \cdot \text{K}$ . This particular

formula, since it requires a trivalent atom to link the two molecules together, will not serve in the case of the lead silicate. A slight modification, however, gives the configuration which follows:

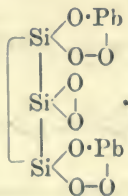


But none of these formulæ fulfils the condition (ii) of p. 1455. In the first five lead compounds, the two oxygen atoms attached to each atom of lead are shown as being similarly situated in the molecule, and should therefore be removed by hydrogen with equal facility. In the last formula, either one or three oxygen atoms should be removed, whereas the actual number withdrawn is two.

The argument developed for the metasilicates is general, and applies, it will be seen, equally well to the present examples. The lead atoms and the removable oxygen atoms being thus found to be each attached to a second oxygen atom, the simplest formulæ deduced are as follows:



Lead trisilicate (polysilicate):



The conclusion to which the foregoing argument leads is also deduced by a somewhat different line of reasoning.

The molecular weight of lead metasilicate is unknown, but the actual molecular formula is probably a multiple, and perhaps a high multiple, of the empirical one. Silica, on account of its difficult volatility, is generally supposed to possess a highly complex molecule. If this is so, the silicate obtained from it by fusion with a limited quantity of lead oxide can hardly be represented by the simple empirical formula. In any case, the silicate  $\text{Pb}_2\text{Si}_3\text{O}_8$  must contain at least three silicon atoms in the molecule, and it will suffice for present

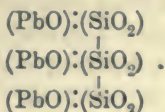
purposes to treble the empirical formula of the metasilicate to compare with this.

Hitherto, by starting with a consideration of the relationship existing between the atoms in the groups  $\text{PbO}$  and  $\text{SiO}_2$ , the following conclusions have been deduced: (1) that the most probable formula is built up with a chain of silicon atoms, and (2) that it is therefore some multiple of the empirical formula.

Conversely, by starting with a multiplied formula, and considering how the members of the multiplied formula are joined together, one is led to the same grouping of the atoms in each member, and to the same structural formula, as already obtained by the first method.

Taking  $n=3^*$  for convenience of discussion, the first of the two fundamental conditions is satisfied by writing  $(\text{PbSiO}_3)_n$  in the form  $(\text{PbO}:\text{SiO}_2)_3$ . The next step is to ascertain how the three members of this formula are joined together.

In this particular case, the basic oxide might conceivably act as the connecting group:  $-\text{Pb}-\text{O}-$ . But the double and complex silicates may contain alkali metals, and the oxides of these metals could not act as connecting groups. Hence, if the formula is to be based on principles of general applicability, the silica groups must be the connecting links. So far, then, one obtains the representation:



The question then arises whether the silica groups are joined by means of their oxygen or their silicon atoms.

If the structure is to be a general one, the connection cannot be by two oxygen atoms, thus:  $^-\text{O}>\text{Si}<\text{O}>\text{Si}<\text{O}>\text{Si}<\text{O}^-$ . For (i) this would exclude any such formula as  $3\text{Na}_2\text{O}, 4\text{SiO}_2$ —that is, any formula which contains more than two  $\text{M}'_2\text{O}$  groups in the molecule. And (ii), since for the reasons previously given it is unlikely that the metal is directly attached to silicon, the structure of the lead silicate corresponding with the above linking must be:



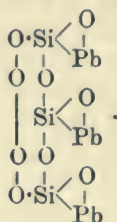
and this does not fulfil condition (ii).

Moreover the linking is probably not effected by *single* oxygen atoms.

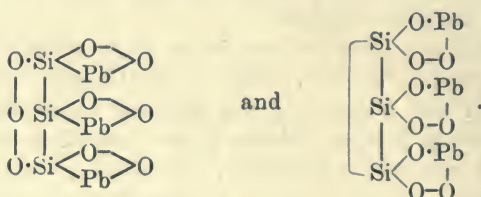
\* It will be seen that the argument does not depend on this arbitrary choice. Any higher value of  $n$  could be adopted.



For the only type of formula which can be constructed to satisfy conditions (i) and (ii) is one in which the lead is attached to silicon :



Hence the oxygen is probably not the connecting atom. If it is not, the silicon must furnish the linking. This being the case, it will be found that the choice lies between the two following formulæ :

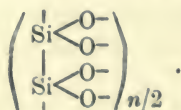


The first of these formulæ being rejected on account of the improbability of the direct connection between the lead and silicon atoms, there remains only the last formula, which is identical with that previously deduced for lead metasilicate.

Reviewing now all those formulæ which have been accepted in this communication as most satisfactorily accounting for the removal of oxygen, it will be seen that these present the following features :

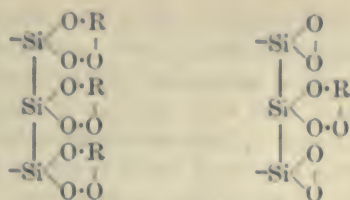
(i) The silicon atoms are in direct combination with each other, and are not joined by means of oxygen.

(ii) To the chain of  $\text{Si}_n$  atoms thus formed, the oxygen corresponding with  $(\text{SiO}_2)_n$  is attached, giving the mode of grouping denoted by :

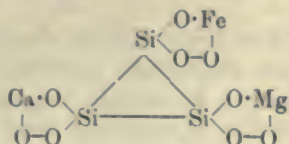


(iii) The oxygen valencies here shown unappropriated are those by which the basic oxides,  $\text{PbO}$ ,  $\text{CuO}$ , &c., are attached to the silicate molecule.

Hence, if these features hold generally, the conception of silicate structure to which they lead is that of a chain, closed or open, of the following type :

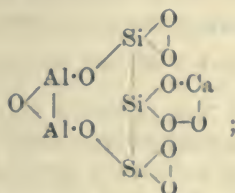


The two silicon valencies here shown as free would presumably be united, the silicate thus forming a closed chain or ring. For example, the pyroxene sahlite,  $\text{CaO}, \text{MgO}, \text{FeO}, 3\text{SiO}_2$ , might be formulated as :

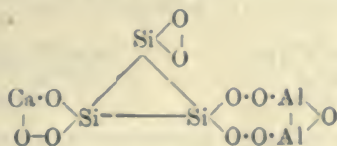


In some cases, the two silicon valencies may possibly be connected by another molecular group, such as  $\text{Al}_2\text{O}_3$ , for instance, again giving a ring: the  $\text{Al}_2\text{O}_3$  would presumably in such cases perform the function of an acid group.

The formula of anhydrous scolecite,  $\text{CaO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2$ , may be given as an illustration :



although, in the absence of any knowledge of the function actually performed by the aluminium oxide, the formula might equally well be one in which this oxide acts as a base :



Lastly, the two valencies in question might conceivably be satisfied by any univalent atoms or groups, without giving rise to a ring.

The structure thus deduced differs from that usually accepted for silicates, wherein the connection between the silicon atoms is always assumed to be made by means of oxygen. But for this latter view, there seems to be little or no direct experimental evidence. It would appear to have been adopted partly from a consideration of the known

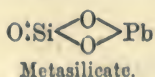
affinity of silicon for oxygen, and partly from the practice of regarding the silicates as salts of hypothetical acids, which latter can be regarded in turn as derivable from orthosilicic acid by the combination of two or more molecules of acid with the loss of one or more molecules of water. But the process, however plausible, is mainly a theoretical one. Definite hydrates of silica are difficult to prepare, and practically nothing is known about their constitution. The arguments are usually based on, or supported by, the analogy with carbon compounds; but a chain or ring of silicon atoms would be equally analogous with the structure shown by carbon derivatives.

It will be noticed that the foregoing discussion has had reference to the lead metasilicate, polysilicate, and disilicate only, and has not included the orthosilicate. As regards the last, it would appear at first sight that the question of structure could hardly arise. Almost beyond question, ethyl orthosilicate must have the structure

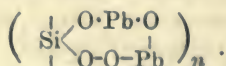


and so also must the orthosilicates of the univalent metals. In the latter case, indeed, there is no alternative; and it would then seem most probable that, with the bivalent and polyvalent metals, the same type of structure occurs, giving, for instance, the accepted formula  $\text{Pb} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{Si} \begin{array}{c} \diagdown \text{O} \\ \diagup \text{O} \end{array} \text{Pb}$  as that of lead orthosilicate.

But, besides the fact that reduction with hydrogen removes only two of the four symmetrical oxygen atoms, there is another experimental result which is difficult to correlate with this formulation. Lead orthosilicate differs from lead metasilicate, polysilicate, and disilicate in this respect, that it leaves on reduction a considerable proportion (although not the whole) of its lead in the metallic state. Now, if the ordinary formulæ of these salts are accepted, they show nothing to account for this difference of behaviour:



A reason for the different deportment is, however, suggested at once when the compounds are formulated on the system indicated above. In this case, the structure of the orthosilicate would be as follows (only one  $\text{Pb}_2\text{SiO}_4$  group being figured):



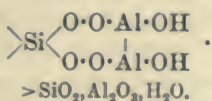
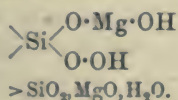
Here the terminal lead atom differs from the other, and from the lead



of the metasilicate, polysilicate, and disilicate, in not being directly attached to the  $\text{SiO}_2$  group. It is possible that this atom is on this account removed from the reduced silicate residue when the compound is heated in hydrogen.

The question now arises, can the various known silicates be formulated on the plan indicated? Most of them certainly can. Moreover, there are certain hitherto obscure points in the behaviour of silicates which appear to be better comprehended and more readily explicable when the silicates are represented in accordance with the principles now put forward.

Thus, it is as a rule possible to include in the formula the combined water, for which in the ordinary system it is often difficult to find a satisfactory place. A molecule of water may be attached to one of the  $\text{>Si<O}$  groups thus:  $\text{>Si<O} \begin{smallmatrix} \text{O} \cdot \text{OH} \\ \text{OH} \end{smallmatrix}$ , the group then appearing as a silicic hydroxide; or it may be attached to the oxide of a bivalent or trivalent metal, the group in this case appearing as the hydroxide of the metal:



The different degrees of tenacity with which different molecules of water are often held in the same silicate may be very well explained on the assumption that the different molecules of water are combined with diverse kinds of oxides. For instance, water removed at a relatively low temperature might be so removed because it was combined with ferric oxide, or with silica itself; that not removed except at high temperatures might be combined with lime, magnesia, or alumina.

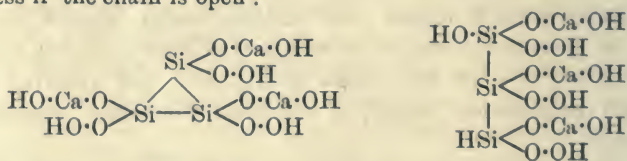
The idea that alumina may replace silica, molecule for molecule, in certain classes of silicates has suggested itself from time to time to various investigators. On the present theory, if such a replacement occurred, it would mean that the alumina enters into the ring or chain forming the framework of the silicate molecule. There is a certain amount of evidence which tends to support the view that this does, in fact, occur. The nature of this testimony may be illustrated by reference to the chlorite group of silicates. No doubt the chlorites are a somewhat ill-defined class of minerals, but they serve very well to bring out the point in question.

According to Dana (*System of Mineralogy*, p. 643), the chlorites yield on ignition 10 to 13 per cent. of water, and in all cases this is probably to be regarded as water of constitution. Now, it will be found that in the chlorites the number of molecules of water is often

exactly equal to, and is never greater than, the sum of the molecules of silica and alumina (or ferric oxide):

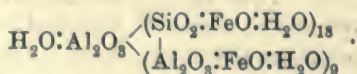
|                       |                    |            |                                      |                   |
|-----------------------|--------------------|------------|--------------------------------------|-------------------|
| Clinochlore.....      | 4H <sub>2</sub> O, | 5(Mg,Fe)O, | 1Al <sub>2</sub> O <sub>3</sub> ,    | 3SiO <sub>2</sub> |
| Prochlorite.....      | 20 "               | 23 "       | 7 "                                  | 13 "              |
| Corundophyllite ..... | 10 "               | 11 "       | 4 "                                  | 6 "               |
| Daphnite .....        | 28 "               | 27FeO      | 10 "                                 | 18 "              |
| Cronstedtite .....    | 3 "                | 3 "        | 1Fe <sub>2</sub> O <sub>3</sub>      | 2 "               |
| Thuringite .....      | 9 "                | 8 "        | 4(Al,Fe) <sub>2</sub> O <sub>3</sub> | 6 "               |
| Strigovite .....      | 2 "                | 2 "        | 1 "                                  | 2 "               |
| Diabantite.....       | 9 "                | 12(Mg,Fe)O | 2Al <sub>2</sub> O <sub>3</sub>      | 9 "               |
| Aphrosiderite .....   | 5 "                | 6 "        | 2 "                                  | 4 "               |
| Delessite .....       | 5 "                | 4 "        | 2 "                                  | 4 "               |
| Rumpfite .....        | 14 "               | 7MgO       | 8 "                                  | 10 "              |

This suggests that the maximum number of molecules of combined water is conditioned by the number of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> groups. By the ordinary method of formulation, it is not easy to see why this should be so; in fact, it is difficult in this way to construct any formula which shall include the whole of the water in some of the above cases. But on the system now suggested the number of molecules of combined water, or, more generally, of the oxides of any univalent element, depends directly on the number of acid groups which go to form the ring or chain. It cannot be greater than this number if a ring is formed, although it might conceivably be one in excess if the chain is open:



But if this be so, then, when the number of molecules of combined water is greater than the number of SiO<sub>2</sub> groups, it can only be because groups other than SiO<sub>2</sub> enter into the ring or chain. Hence the coincidence of the numbers of water molecules with the sum of the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> groups in the foregoing cases indicates that the Al<sub>2</sub>O<sub>3</sub> in these chlorites enters into the ring, and to this extent performs the same functions as the SiO<sub>2</sub> groups.

As an illustration we may take the mineral daphnite, the empirical formula of which is given by Dana as H<sub>56</sub>Fe<sub>27</sub>Al<sub>20</sub>Si<sub>18</sub>O<sub>121</sub>. This corresponds with 28H<sub>2</sub>O, 27FeO, 10Al<sub>2</sub>O<sub>3</sub>, 18SiO<sub>2</sub>, and would be concisely formulated as follows:



The other chlorites can be formulated in a similar manner.

For convenience, the foregoing general argument has been developed with especial relation to lead silicates. It applies, however, equally well, *mutatis mutandis*, to all silicates wherein the basic element is a metal which forms an easily reducible oxide, in so far as this property is retained after the oxide is incorporated in the silicate. As regards the silicates of other metals, some reasons have already been adduced to show that the oxides of these metals are probably to be considered as taking the same positions as the reducible oxides in the building up of the silicate molecule. Hence it is possible that the foregoing structure may, more or less generally, hold good as a type of the usual arrangement of atoms in silicates. Whether this is the rule or the exception is a matter for future experiment to decide. There may be great diversity of structure with the silicates as with carbon compounds. And that some diversity does, in fact, exist, is shown by the behaviour of those silicates which, although containing iron, are not reduced by hydrogen at a red heat. It need not, however, be assumed that this refractory deportment is incompatible with the essential structure deduced from the experiments on the reducible silicates. It may be possible to formulate such refractory silicates on the general plan in question, but so that all the oxygen of the  $\text{Fe}_2\text{O}_3$  groups is directly connected either with silicon or with aluminium, the difficulty of reduction thus becoming explicable.

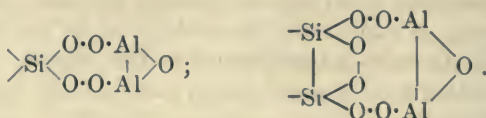
On the other hand, such instances as these may point to an essentially different constitution for the refractory silicates. There does not seem to be any immediate prospect of definite proof in this and similar problems of silicate structure; but in any case, the deductions drawn from the simple experiments now cited may furnish at least a clue to the elucidation of the matter, and they are therefore offered as a contribution towards the study of the question.

*Addendum.*—A few examples are added to illustrate the formulation of various classes of silicates after the manner described in the foregoing pages. The empirical formulæ are taken from Dana's "System of Mineralogy."

It will, of course, be understood that the structural forms given are not to be regarded as proved formulæ, since nothing whatever is known about the positions of the various groups. They are merely put forward to show that it is possible to represent even the more complicated silicates on the principles explained, and to do so with comparative simplicity. In the present state of our knowledge, however, a certain amount of assumption is unavoidable. For example, a molecule of alumina may in any given case either form part of the silicate nucleus or ring, presumably then acting as an



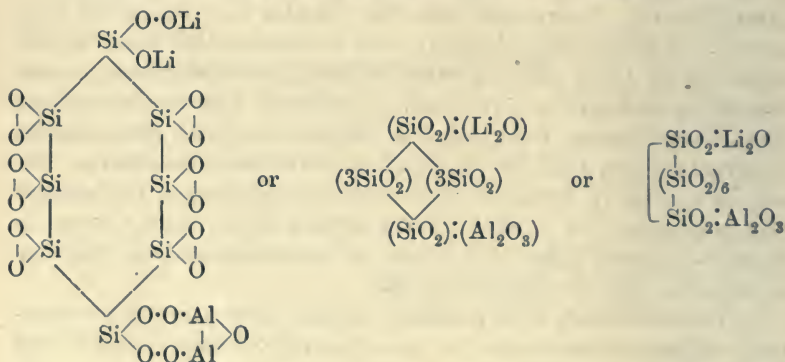
acidic group, or it may serve to join two nuclei, and thus appear as an intermediate or neutral oxide; or, again, it may act as a basic oxide, in which case it may be connected either with one or with more  $\text{SiO}_2$  groups:



### I. Disilicates and Polysilicates.

#### *Petalite Group.*

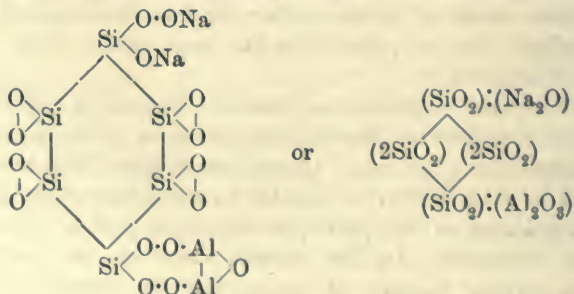
*Petalite*,  $\text{LiAl}(\text{Si}_2\text{O}_5)_2$ , on doubling =  $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 8\text{SiO}_2$ :



After one or two illustrative examples the shorter methods of writing the formulæ will be used.

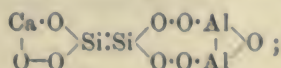
#### *Felspar Group.*

*Albite*,  $\text{NaAlSi}_3\text{O}_8$  or  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, \text{SiO}_2$ :

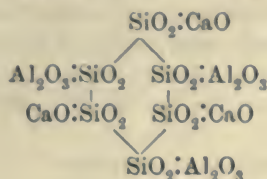


*Anorthite*,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , or  $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$

The structural formula of this may be written to agree with the empirical one, as :

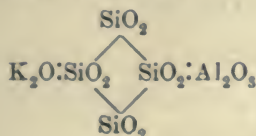


or it may be trebled to compare with *albite* and *orthoclase* :

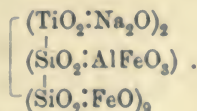


## II. Metasilicates.

*Leucite*,  $\text{KAl}(\text{SiO}_3)_2$ , or  
 $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2 :$

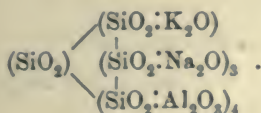


*Enigmatite*,  
 $2\text{Na}_2\text{O}, 9\text{FeO}, \text{AlFeO}_3, 12(\text{Si}, \text{Ti})\text{O}_2 :$

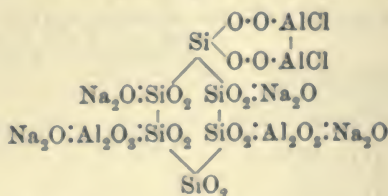


## Orthosilicates.

*Nephelite*,  $\text{K}_2\text{Na}_6\text{Al}_8\text{Si}_9\text{O}_{34}$ , or  
 $\text{K}_2\text{O}, 3\text{Na}_2\text{O}, 4\text{Al}_2\text{O}_3, 9\text{SiO}_2 :$

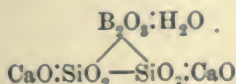


*Sodalite*,  $\text{Na}_4(\text{AlCl})\text{Al}_2(\text{SiO}_4)_3$ ,  
or  $4\text{Na}_2\text{O}, 2\text{Al}_2\text{O}_3, \text{Al}_2\text{O}_3\text{Cl}_2, 6\text{SiO}_2 :$

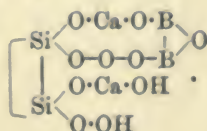


## Basic Orthosilicates.

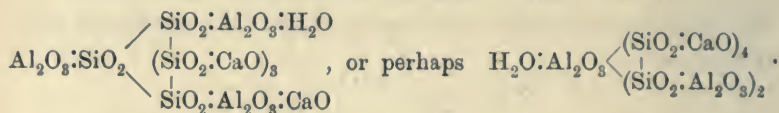
*Datolite*,  $\text{HCaBSiO}_5$ , =  $\text{Ca}(\text{B} \cdot \text{OH})\text{SiO}_4$  (Groth),  
or  $\text{H}_2\text{O}, 2\text{CaO}, \text{B}_2\text{O}_3, 2\text{SiO}_2 :$



or



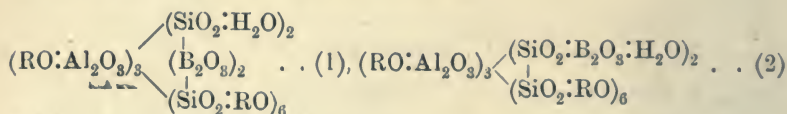
*Zoisite*,  $\text{Ca}_2(\text{Al}\cdot\text{OH})\text{Al}_2(\text{SiO}_4)_3, 4\text{CaO}, 3\text{Al}_2\text{O}_3, 6\text{SiO}_2, \text{H}_2\text{O}$  :



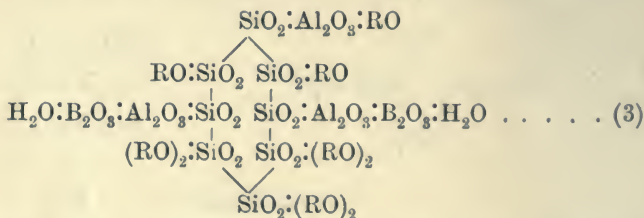
### Subsilicates.

*Tourmaline*.—Penfield and Foote's formula (*Amer. Chem. J.*, 1899, [iv], 7, 118), when doubled, gives:  $9(\text{Mg}, \text{Ca}, \&c.)\text{O}, 3\text{Al}_2\text{O}_3, 2\text{B}_2\text{O}_3, 2\text{H}_2\text{O}, 8\text{SiO}_2$ ; the last four terms being common to all varieties of tourmaline, and  $\text{Al}_2\text{O}_3$  replacing a portion of the RO groups isomorphously in some specimens.

The following are alternative structures :

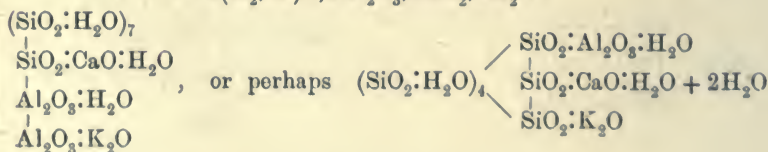


and

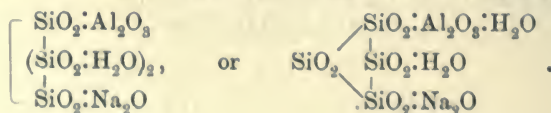


### Zeolites.

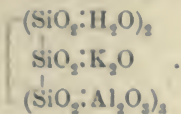
*Phillipsite*,  $(\text{K}_2, \text{Ca})\text{Al}_2\text{Si}_4\text{O}_{12}, 4\frac{1}{2}\text{H}_2\text{O}$ , or  
 $2(\text{K}_2, \text{Ca})\text{O}, 2\text{Al}_2\text{O}_3, 8\text{SiO}_2, 9\text{H}_2\text{O}$  :



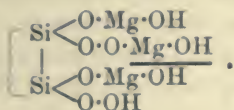
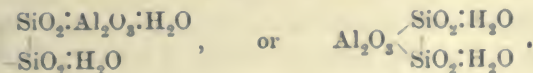
*Analcite*,  $\text{NaAl}(\text{SiO}_3)_2, \text{H}_2\text{O}$ , or  $2\text{H}_2\text{O}, \text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$  :





*Mica Group.**Muscovite*,  $H_3KAl_3(SiO_4)_3$ , or  $2H_2O, K_2O, 3Al_2O_3, 6SiO_2$  :*Serpentine and Talc Group.**Serpentine*,  $H_4Mg_3Si_2O_9$ , or  $2H_2O, 3MgO, 2SiO_2$ .

Clarke and Schneider write the formula as  $H_3(Mg \cdot OH)Mg_2(SiO_4)_2$ , because a portion of the magnesium is converted into chloride when the silicate is heated in hydrogen chloride. In the following formula, the underlined  $MgOH$  group differs from the other two in its mode of attachment, and this may be the group removed by the action of hydrogen chloride.

*Kaolin Group.**Kaolinite*,  $H_4Al_2Si_2O_9$ , or  $2H_2O, Al_2O_3, 2SiO_2$  :

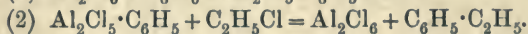
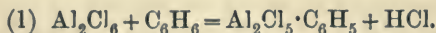
In conclusion, the author desires to acknowledge his indebtedness to Dr. T. E. Thorpe, C.B., F.R.S., for permission to utilise experimental results obtained in the Government Laboratory.

GOVERNMENT LABORATORY,  
LONDON.

## CXLII.—A *Dynamical Study of the Friedel-Crafts Reaction.*

By BERTRAM D. STEELE, D.Sc.

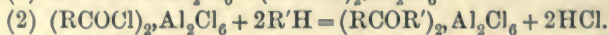
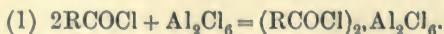
SINCE the discovery, in 1871, by Friedel and Crafts of the well-known synthesis which bears their name, many attempts have been made to explain the influence of the aluminium chloride. The discoverers, in their early papers, explained the reaction between benzene and an alkyl chloride by assuming that an intermediate compound was alternately produced and decomposed, as is shown in the following equations:



No conclusive proof of the existence of the intermediate compound was advanced, and although certain experiments carried out in the course of the present research seem to indicate its formation in small quantity, the evidence is scanty and inconclusive, and some more satisfactory explanation of the mechanism of the reaction is needed. One point in which the aluminium chloride seems, in these reactions, to differ fundamentally from the so-called catalysts is that a small quantity is not sufficient to induce reaction between large quantities of reagents; and this difference in behaviour has not yet been satisfactorily explained.

The preparation of a ketone from a hydrocarbon and an acid chloride is the only one of the numerous types of reaction brought about under the influence of aluminium chloride that is at all clearly understood.

Perrier (*Ber.*, 1900, 33, 815) and Boeseken (*Rec. trav. chim.*, 1900, 19, 19; *ibid.*, 1901, 20, 102) have brought forward the view that such reactions take place according to the following scheme.



They have isolated crystalline compounds of aluminium chloride with the acid chloride, and with the ketone. Kronberg (*J. pr. Chem.*, 1900, ii, 61, 494) attempts to assign constitutional formulæ to these compounds in order to explain their reactions, and Kohler (*Amer. Chem. J.*, 1900, 24, 385) has determined the molecular weights in solution of the analogous aluminium bromide compounds, and finds that they correspond with the foregoing formulæ.

Other investigators have recorded the existence of various compounds of aluminium chloride with different organic substances; thus, Gustavson (*Chem. Centr.*, 1883, 14, 344) refers to the compounds of aluminium bromide with benzene and toluene. Combes (*Compt. rend.*, 1886, 103, 814) describes a compound of aluminium chloride and acetyl chloride having the formula  $\text{Al}_2\text{Cl}_6(\text{CH}_3\cdot\text{COCl})_6$ , and Konowaloff and Plotnikoff (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 1020; *Abstr.*, 1900, i, 323) describe a whole series of such compounds.

In the case of ferric chloride, Nencki (*Ber.*, 1899, 32, 2414) has described a somewhat complicated compound, which appears to contain ferric chloride, acid chloride, and ketone; and Gurewitsch (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 625) explains the synthesis of keto-phenols by a series of reactions depending on the formation of intermediate compounds containing ferric chloride.

For the synthesis of hydrocarbons, no satisfactory explanation has been hitherto advanced.

If the ketone synthesis is conditioned by the occurrence of intermediate compounds which can be easily isolated, the fact that the isolation of similar compounds in other cases is difficult or impossible is no evidence of their non-existence, and it is probable that the formation of such compounds is a necessary condition of the Friedel-Crafts reaction.

Aluminium chloride as a condensing agent usually behaves in such a way that there is a definite relationship between the amount of substance formed and the amount of chloride used. In some instances, a large quantity of the latter is required to bring about condensation, and in others the quantity is so small that the reaction partakes of the nature of catalysis, and the latter condition seems to obtain more generally when ferric chloride is employed.

This apparently fundamental difference of behaviour is probably dependent on and explained by the formation, or non-formation, of a compound of the aluminium (or ferric) chloride with the product of the reaction, and on the stability or degree of dissociation of this compound.

Two extreme cases may be considered.

(1) The compound of aluminium chloride and final product is perfectly stable or non-dissociable; (2) complete dissociation takes place, or no compound at all is formed. In the former case, if the compound is assumed to be one in which the two components are present in equivalent proportions, then every gram-equivalent of reagent (acid chloride, for example) would, in the presence of an excess of the second reacting substance, require one gram-equivalent of the aluminium or ferric chloride to bring about complete reaction. In the second case, where complete dissociation occurs, the metallic

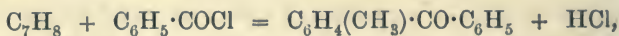


chloride should behave as a true catalyst, since it would be constantly regenerated, and the quantity present would influence only the velocity of the reaction. In intermediate cases, where the final compound with metallic chloride may be partially dissociated, it must necessarily follow that the greater the extent of this dissociation the less chloride will be required to bring about reaction between a given quantity of reacting substances.

Friedel and Crafts have shown that, besides the synthetical, there is also a disruptive action induced by aluminium chloride; as, for instance, the decomposition of toluene into benzene and methyl chloride in the presence of an excess of hydrogen chloride, and it is probable that many more of these reactions are reversible, a fact which, if recognised, would go far to explain not only the poor yields, but also the extremely complicated and unexpected compounds which are sometimes obtained.

The course of certain reactions of the type under discussion has been followed in the present paper, and, in order to avoid complications as far as possible, two reactions have been selected for examination which appear to progress at a measurable rate until they are quite complete. The reactions which have been studied are those represented by the following equations:

(1) Ketone synthesis,



under the influence of (a) aluminium chloride; (b) ferric chloride.

(2) Hydrocarbon synthesis,



under the influence of the same two reagents.

### *Preparation of the Reagents.*

On account of the well-known difference in the behaviour of various samples of aluminium chloride in the Friedel-Crafts reaction, considerable care was taken in the preparation and preservation of this reagent.

A large quantity, prepared by the action of dry hydrogen chloride on aluminium turnings at a dull red heat, was placed in a carefully dried combustion tube, and distilled twice in a current of pure hydrogen, which had been dried by passing through sulphuric acid and finally over a layer of phosphoric anhydride about 40 cm. long. The product was then rapidly removed to a desiccator containing phosphoric oxide.

But even with all precautions it was found impossible during

weighing to avoid the absorption of water in varying amounts by aluminium chloride, and consequently the value of the velocity constant in different experiments shows a slight variation. This difficulty was not encountered to the same extent with ferric chloride, which was prepared by the action of chlorine on iron turnings, redistilled in a current of carbon dioxide, and preserved in a desiccator containing phosphoric oxide. Although this substance is also extremely hygroscopic, the presence of a minute amount of water does not appear to have such an influence on the velocity of reaction.

The toluene employed was obtained from Kahlbaum, and had a constant boiling point; it was distilled from sodium and also kept over this metal.

### *The Method of Experiment.*

Owing to two disturbing causes, namely, the presence of a solid phase, which necessitates constant and rapid stirring, and the solubility of hydrogen chloride in toluene, it is not possible, in following the course of the reactions, to measure the pressure of the evolved gas, although this method has met with considerable success in other cases.

The apparatus employed (Fig. 1, p. 1474) consists of a double bubbler, *A*, and an absorption vessel, *B*. The reaction mixture was placed in the tube *c*, and an equal volume of toluene in the tube *d*. The exit tube, *b*, was connected by means of india-rubber tubing with the side-tube of *B*, the capillary tube, *e*, dipping under mercury to prevent the water in *B* finding its way into the vessel, *A*. Hydrogen entering the apparatus through the tube *a* became saturated with toluene while passing through *d*, whence it passed through *c*, carrying the generated hydrogen chloride into *B*, where it was absorbed and titrated.

In performing an experiment, after the toluene and the reaction-mixture of toluene and acid chloride had been placed in *d* and *c* respectively and all the air had been displaced by a current of hydrogen, a weighed quantity of aluminium chloride was introduced through *g* at a given moment, and readings were made of the time elapsed and the alkali used in titration. The whole apparatus was immersed in a thermostat at a temperature of  $25.0^{\circ} \pm 0.02^{\circ}$ .

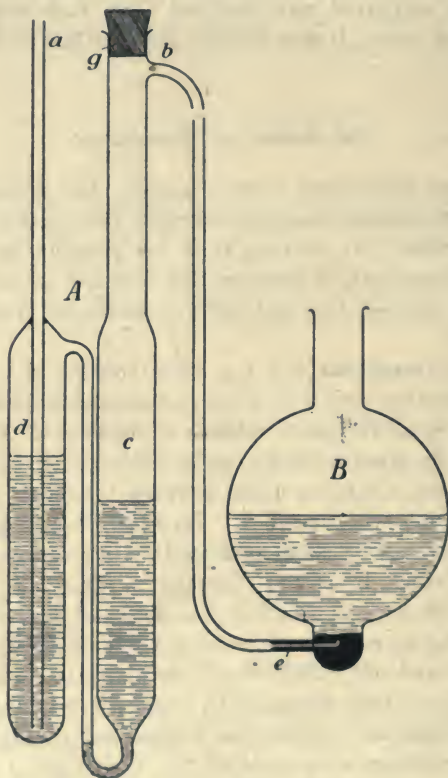
In the majority of experiments, the chief difficulty to be overcome was the solubility of the acid in toluene. This will be dealt with later, but in a few cases, on account of the extreme slowness of the reaction, the solvent could, without error, be regarded as containing no dissolved hydrogen chloride.

In these cases, considerable difficulty was experienced in maintaining a current of hydrogen at the required rate for the necessary time,

and it may be of interest to describe briefly how this difficulty was finally overcome.

The hydrogen was obtained by the electrolysis of sulphuric acid in a battery of seven U-tubes arranged in series. When a current of about 4 amperes is passed through such a series, the concentration of the acid is altered by the passage of the hydrogen ions to the cathode, and of the sulphate ions to the anode, in such a way that it becomes

FIG. 1.



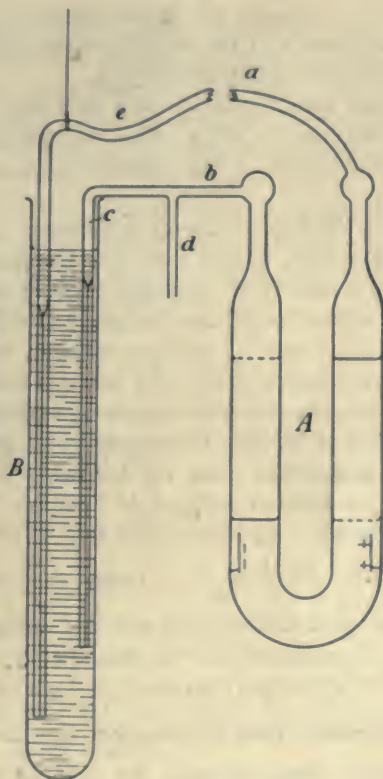
very dilute at the cathode and very concentrated at the anode, and since the concentration used was that of maximum conductivity, the latter from both changes becomes very much reduced. In one experiment, the current fell from 4 amperes to 1 in the course of 5 hours. It was therefore necessary to stir the contents of the seven U-tubes, and this was successfully accomplished by means of the apparatus shown diagrammatically in Fig. 2 (p. 1475).

In the figure, which shows only one U-tube, the hydrogen escapes



by the tube *b*, which branches into the two tubes *c* and *d*; *d* leads to the drying tubes, and from them to the apparatus shown in Fig. 1. The tube ends in a capillary tube, dipping under water in the long tube, *B*. By regulating a stop-cock and screw clip on the branch (not shown in the diagram), it is easy to allow about one or two bubbles of hydrogen per second to escape from *c*, thus maintaining a constant pressure on the gas escaping through the bubblers.

FIG. 2.



The whole of the oxygen escapes through *a*, the two parts, *a* and *c*, of which are connected by a flexible glass spiral, not shown in the figure, made of 3 metres of very thin quill tubing.

The delivery tube, *c*, is attached to a cord passing over a pulley, the other end of the cord being fastened to an arm soldered to the bearer of the minute hand of a small clock, and by the movement of this arm a vertical motion is imparted to *c*, of such a nature that it moves once up and down every hour. As a result of this movement, the

escaping pressure of the oxygen is constantly varying, being alternately greater and less than that of the hydrogen, which remains constant, and the level of the liquid in the two limbs of *A* (and also the remaining six electrolytic cells) is also continually varying, taking up alternately the extreme positions represented by the plain and dotted lines. In this way, very effective mixing is brought about, the above mentioned changes in concentration cannot occur, and it has been found possible to maintain a steady current of hydrogen corresponding with 4 amperes for over 72 hours.

The flexible spiral already mentioned cannot be replaced by india-rubber tubing on account of the rapidity with which this is destroyed by the ozone generated during electrolysis.

A trace of ozone also found its way into the escaping hydrogen (probably by solution in the acid). This was got rid of by passing the gas through a set of Geissler's bulbs containing a solution of potassium iodide.

*The Solubility of Hydrogen Chloride in Toluene.*—In the treatment of the experimental results, it has been found necessary to introduce a correction for the solubility of hydrogen chloride in the liquid. Since the composition of the latter varied slightly in different experiments, and also during the course of each experiment, but consisted always for the most part of toluene, it has been assumed that the solubility was the same as in pure toluene, an assumption involving an unimportant error. The method of treating the results and applying the correction will be clearly understood from the following considerations. The desaturation of a saturated solution of hydrogen chloride in toluene by a steady current of hydrogen will follow the course of a unimolecular reaction,  $K = \frac{1}{T} \log \frac{a}{a-x}$ , where  $a$  is the amount of gas contained in the saturated solution and  $x$  is the amount carried away in the time  $T$ . The value of  $K$  will depend only on the rate at which the indifferent gas (hydrogen) is passed through the solution.

From the differential form of the above equation,  $a-x = \frac{1}{K} \frac{dx}{dt}$ , it is possible to calculate at any moment the value of  $(a-x)$ , which is the amount of hydrogen chloride remaining dissolved. The quantity of hydrogen chloride produced by a reaction in a given time is obviously equal to that which has been carried away by the hydrogen and titrated, *plus* the small amount remaining dissolved in the toluene, and the latter value  $(a-x)$  is given by the above equation, where  $K$  is the constant for the desaturation curve when obtained with the same current of hydrogen per second as that used in the velocity experiments, and  $dx/dt$  is the tangent to the curve at the time of observation.

The same result is attained graphically by superposing the curve of

a given reaction on the desaturation curve and reading off the values of  $(a - x)$  from the latter. Both methods give the same value for the correction within a very small limit of error. The experimental results given below have been treated in the latter manner, and the figures given in the tables are the corrected ones, that is to say, the titration results *plus*  $(a - x)$ .

## EXPERIMENTAL.

The following experiments were carried out using a current of hydrogen developed in seven electrolytic cells arranged in series by an electric current of  $4.7 \pm 0.1$  amperes, equivalent to 3.81 c.c. of hydrogen per second. The acid liberated was titrated by a solution of sodium hydroxide free from carbonate, equivalent to 0.00864 gram of hydrogen chloride per c.c. In order to simplify the type of the reactions by making the active mass of one of the reacting substances constant, a large excess of toluene has been used in all cases.

In the following table are given the figures for the desaturation curve of hydrogen chloride in toluene.

TABLE I.

Twenty c.c. of toluene saturated with hydrogen chloride at  $25^\circ$  dissolve 0.2902 gram of the gas.

$T$  = time in minutes,  $x$  = no. of c.c. of NaOH neutralised,  $a = 33.6$ .

| $T$ .    | $x$ . | $K = \frac{1}{T} \log \frac{a}{a-x}$ . |
|----------|-------|--|
| 0.1      | 4.3   | —                                      |
| 1.2      | 27.5  | 1.43                                   |
| 2.0      | 31.8  | 1.47                                   |
| 2.75     | 32.9  | 1.43                                   |
| 3.1      | 33.3  | 1.52                                   |
| 5.0      | 33.5  | —                                      |
| $\infty$ | 33.6  | —                                      |
|          |       | Mean                                   |
|          |       | 1.46                                   |

*Ketone Synthesis.*

(a) *The Reaction between Benzoyl Chloride and Toluene in the presence of Aluminium Chloride.*

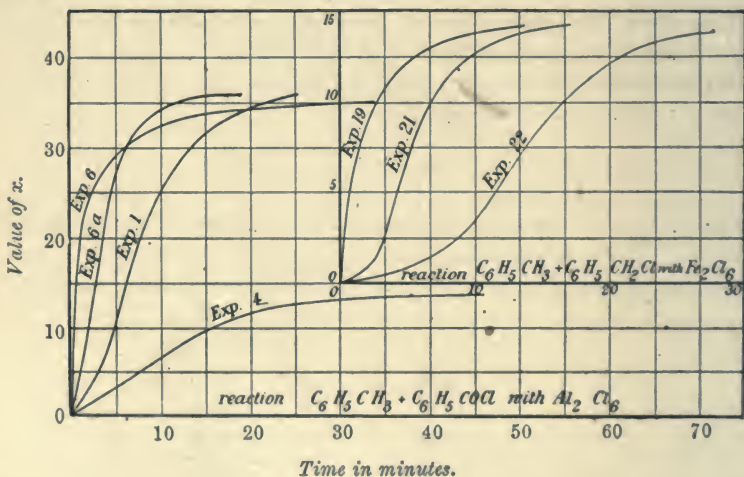
It was expected that this would be a unimolecular reaction, but it was very soon found that its order varied in a remarkable manner with the ratio of aluminium chloride to acid chloride: On this account, and



also because of the varying influence on the velocity exerted by different samples of aluminium chloride, each experiment has been frequently repeated, and, although the actual values of  $K$  varied slightly, the type of reaction with a given ratio remained uniform.

Four series of experiments have been carried out in which the ratio of aluminium chloride to acid chloride was respectively 0.65, 1.00, 1.3, and 2.3, the results of which are given in tables II—V. In these and the other tables which are given,  $K_1$  and  $K_1'$  represent the values of the constant calculated from the equation for a unimolecular reaction,  $K = \frac{1}{T} \log \frac{a}{a-x}$ , in which  $a$  = the total quantity of hydrogen chloride that can be produced if the reaction becomes com-

FIG. 3.



pleted, and  $x$  = the amount produced in the time  $T$ .  $K_1$  and  $K_1'$  differ from each other in that, for the calculation of  $K_1$ ,  $a$  is the total amount of the gas producible, and  $T$  is measured from the actual time of starting the experiment, whilst for the calculation of  $K_1'$ ,  $a'$  represents the amount of hydrogen chloride that can be produced from the substances remaining unchanged at some arbitrarily selected time  $T'$ .

$K_2$  and  $K_2'$  represent the values of the constant calculated from the equation for a bimolecular reaction,  $K_2 = \frac{1}{T} \cdot \frac{x}{a(a-x)}$ , and differ from each other in the same manner as  $K_1$  and  $K_1'$ .

The results of these series are also plotted in Fig. 3, where the changes in the form of the curve with different ratios are very clearly shown.

TABLE II (Experiment 1).—Aluminium chloride = 0.73 gram. Benzoyl chloride = 1.18 grams; ratio = 0.65. Toluene = 20 c.c.  $\alpha = 35.4 \times 0.65 = 23.0$ .

| $T$ . | $\alpha$ . | $K_1 \times 10^3$ . | $\alpha/T$ . |
|-------|------------|---------------------|--------------|
| 3     | 4.3        | 69                  | —            |
| 5     | 10.4       | 97                  | 2.08         |
| 7     | 14.5       | 143                 | 2.07         |
| 9     | 16.9       | 146                 | 1.88         |
| 11    | 18.3       | 145                 | 1.66         |
| 13    | 19.3       | 141                 | —            |
| 15    | 20.0       | 136                 | —            |
| 21    | 21.1       | 120                 | —            |
| 31    | 21.8       | —                   | —            |
| 52    | 22.2       | —                   | —            |
| 1080  | 23.0       | —                   | —            |

Ratio of aluminium chloride to ketone formed = 1.0.

TABLE III (Experiments 2, 3, and 4).—Aluminium chloride = 1.2 grams. Benzoyl chloride = 1.18 grams; ratio = 1.0. Toluene = 20 c.c.  $\alpha = 35.4$ .

*Experiment 2.*

| $T$ . | $\alpha$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $\alpha/T$ . |
|-------|------------|---------------------|----------------------|--------------|
| 4     | 6.6        | 51.8                | $(T' = T - 9)$       | —            |
| 7     | 16.4       | 88.4                | $(\alpha' = 19.0)$   | 2.34         |
| 9     | 21.0       | 100                 | —                    | 2.33         |
| 11    | 27.1       | 134                 | 208                  | 2.47         |
| 13    | 30.2       | 147                 | 217                  | 2.31         |
| 15    | 32.1       | 158                 | 219                  | 2.13         |
| 17    | 33.2       | 164                 | 214                  | 1.95         |
| 19    | 33.9       | 166                 | 210                  | —            |
| 21    | 34.4       | 171                 | 211                  | —            |
| 23    | 34.6       | 166                 | 198                  | —            |
| 25    | 34.8       | 164                 | —                    | —            |

Mean [211]

*Experiment 3.*

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 1.25  | 4.9   | 118                 | $(T' = T - 4.5)$     | —       |
| 2.75  | 9.3   | 113                 | $(a' = 20.0)$        | 3.38    |
| 3.75  | 13.1  | 123                 | —                    | 3.50    |
| 4.5   | 15.4  | 127                 | —                    | 3.43    |
| 6.5   | 21.4  | 143                 | 180                  | 3.30    |
| 7.75  | 24.9  | 157                 | 194                  | 3.23    |
| 10.0  | 28.1  | 158                 | 184                  | 2.81    |
| 13.25 | 31.8  | 173                 | 196                  | —       |
| 15.0  | 32.9  | 176                 | 198                  | —       |
| 16.0  | 33.4  | 180                 | 200                  | —       |
| 18.0  | 34.1  | 184                 | 202                  | —       |
| 21.0  | 34.6  | 181                 | 196                  | —       |
| 26.0  | 35.1  | 183                 | 195                  | —       |

Mean [194]

Experiment 4 yields a curve of exactly the same type.  $K_1' \times 10^3 = 168$ .

*Experiment 5.* Aluminium chloride = 0.47 gram. Benzoyl chloride = 0.46 gram; ratio = 1.0. Toluene = 20 c.c.  $a = 14.1$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 2     | 1.45  | 51                  | $(T' = T - 9)$       | 0.72    |
| 3     | 2.05  | 52                  | $(a' = 7.65)$        | 0.68    |
| 5     | 3.50  | 57                  | —                    | 0.70    |
| 7     | 4.9   | 61                  | —                    | 0.70    |
| 9     | 6.45  | 68                  | —                    | 0.713   |
| 12    | 8.35  | 74                  | 95                   | 0.70    |
| 14    | 9.45  | 79                  | 99                   | 0.675   |
| 17    | 10.7  | 83                  | 103                  | 0.63    |
| 19    | 11.35 | 86                  | 104                  | 0.60    |
| 23    | 12.2  | 87                  | 103                  | —       |
| 27    | 12.8  | 83                  | 100                  | —       |
| 32    | 13.1  | 83                  | 90                   | —       |
| 42    | 13.6  | 80                  | —                    | —       |

Mean [99]



TABLE IV (Experiments 6a, 7a, and 10).

*Experiment 6a.*

Benzoyl chloride = 1.19 grams, added to the reaction mixture of Experiment 6, after the reaction had entirely ceased.  $\alpha = 35.4$ ; ratio = 1.3.

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 2.25  | 12.45 | 196                 | $(T' = T - 4.25)$    | 5.54    |
| 3.25  | 18.65 | 230                 | $(\alpha' = 11.7)$   | 5.71    |
| 4.25  | 23.7  | 261                 | —                    | 5.59    |
| 5.25  | 27.9  | 296                 | 445                  | 5.32    |
| 6.25  | 31.1  | 323                 | 503                  | 4.98    |
| 7.25  | 32.9  | 369                 | 520                  | —       |
| 8.25  | 33.8  | 376                 | 493                  | —       |
| 10.25 | 34.8  | 327                 | 496                  | —       |

Experiment 7a gave a curve identical with 6a.

In experiment 10, the reaction mixture, which was freshly prepared, contained no ketone; it also gave the same curve as 6a.

TABLE V (Experiments 6, 7, 8, and 9).

*Experiment 6.*

Aluminium chloride = 2.56 grams. Benzoyl chloride = 1.18 grams; ratio = 2.3. Toluene = 20 c.c.  $\alpha = 35.4$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_2 \times 10^4$ . | $x/T$ . |
|-------|-------|---------------------|---------------------|---------|
| 1.25  | 12.6  | 353                 | —                   | 10.0    |
| 2.0   | 22.5  | 466                 | 229                 | 11.5    |
| 2.5   | 24.8  | 480                 | 264                 | 9.9     |
| 3.0   | 26.4  | 460                 | 276                 | 8.8     |
| 3.5   | 27.5  | 428                 | 281                 | —       |
| 4.0   | 28.3  | 402                 | 281                 | —       |
| 5.0   | 29.2  | 348                 | 266                 | —       |
| 6.0   | 30.1  | 316                 | 269                 | —       |
| 7.75  | 31.3  | 279                 | 278                 | —       |
| 9.0   | 31.9  | 256                 | 285                 | —       |
| 11.75 | 33.7  | 258                 | [452]               | —       |
| 23.25 | 34.5  | 155                 | [465]               | —       |
| 37.5  | 35.1  | 127                 | [885]               | —       |

Mean [270]

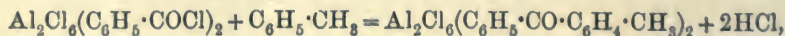
Experiments 7, 8, and 9 (ratios 2.2, 2.3, and 2.4) gave results in close agreement with the above.

It will be seen that the phenomenon of chemical induction or initial acceleration is manifested to a greater or less extent in all the experiments recorded, being much more marked in those in which the ratio of aluminium chloride to acid chloride is small. In the experiments in Tables II and III, this induction effect is shown by the gradual increase of  $K_1$  from a small value to a maximum, at which it remains practically constant until the reaction is completed. During the first portion of the reaction, the amount of hydrogen chloride evolved is very nearly directly proportional to the time, or  $x/T$  is constant, and from the time at which this begins to be no longer the case, the reaction becomes unimolecular, as is shown by the constancy of  $K_1'$ , and the time at which the reaction first begins to be unimolecular corresponds with that at which the aluminium chloride disappears as a solid phase.

In the experiments (Table V) in which the ratio of aluminium chloride to benzoyl chloride was increased to 2.3,  $K_1$  (apart from a slight initial rise due to the induction effect), instead of increasing, steadily decreases in value. On the other hand,  $K_2$  is very nearly constant for the greater part of the reaction, which is bimolecular under the conditions of these four experiments.

The foregoing results are best explained by assuming that the reaction between toluene and benzoyl chloride is conditioned by the previous formation of a compound or compounds of one or both of the reacting substances with aluminium chloride, and that the latter is withdrawn from the system as a component of a final compound with the ketone produced.

When the ratio of aluminium chloride to benzoyl chloride is unity or less, the scheme of reaction suggested by Perrier and Boeseken is sufficient to explain all the facts. Thus, if the first stage consists in the formation of the compound of the aluminium and acid chlorides, which reacts with the toluene according to the equation,



then the reaction cannot be unimolecular, if considered from the time the substances are first mixed, since the concentration of the  $\text{Al}_2\text{Cl}_6(\text{C}_6\text{H}_5\cdot\text{COCl})_2$  must necessarily rise from zero to a constant value, which will depend on the solubility of the compound in toluene, and at which it will remain so long as both aluminium chloride and benzoyl chloride are present.

For that portion of the reaction during which its concentration does not vary, the active mass of the two reacting substances, namely,  $\text{Al}_2\text{Cl}_6(\text{C}_6\text{H}_5\cdot\text{COCl})_2$  and toluene, is constant, and this is the condition necessary in order that  $x$  may be proportional to  $T$ . From the time when either of the chlorides has disappeared, the concentration of the intermediate compound is no longer maintained at a constant value

the reaction becomes unimolecular, and from this point  $K_1'$  is constant.

From the result of the experiment described in Table II, in which one gram-equivalent of aluminium chloride fails to cause more than one gram-molecule of benzoyl chloride to undergo condensation with toluene, it is evident that the aluminium chloride enters into very stable combination with the ketone. For if this compound were appreciably dissociated, the regenerated aluminium chloride would immediately combine with the unchanged benzoyl chloride, giving rise to more ketone and consequent liberation of more hydrogen chloride.

The foregoing scheme does not explain the change in the order of the reaction brought about by increasing the amount of aluminium chloride; and the presence of an additive compound of aluminium chloride and toluene, such as that referred to by Gustavson, appears to be indicated.

If the benzoyl chloride and toluene both form intermediate compounds containing aluminium chloride, which then interact with elimination of hydrogen chloride, the reaction becomes bimolecular, and  $K_2$  becomes constant, provided that the concentration of the two substances happens to be very nearly the same, a condition which appears to be satisfied when the ratio of aluminium chloride to benzoyl chloride is 2.3. In experiments with this ratio, an excess of aluminium chloride always remained after the reaction was completed, and in order to ascertain whether the products of the reaction exerted any influence, a further quantity of benzoyl chloride was added to the reaction mixture from experiments 6 and 7. A parallel experiment (No. 10), in which the ratio was the same, namely, 1:3, was also carried out, and as a result (Table IV) it was found that the presence of the ketone had no influence on the course of the reaction, which, with this ratio, is unimolecular in its last stages.

(b) *The Reaction between Benzoyl Chloride and Toluene in the presence of Ferric Chloride.*

From the fact, already mentioned, that Nencki has, in the study of this reaction, isolated compounds containing ferric chloride, which are more or less analogous with those containing aluminium chloride, it was anticipated that the reaction would proceed in a similar manner to the one just considered. A number of experiments have been carried out, using different ratios of ferric chloride to benzoyl chloride, with the result that only when this is unity is it possible to calculate any satisfactory constant, and with this ratio the reaction is bimolecular.

The results of two experiments, Nos. 11 and 12, in which the ratios



were respectively 0.91 and 1.0, are given in Table VI. In both these experiments,  $K_1$  diminishes rapidly in value as the reaction proceeds, a behaviour which indicates that the reaction is of a higher order than unity;  $K_2$ , on the other hand, is constant.

TABLE VI (Experiment 11).—Ferric chloride = 1.25 grams. Benzoyl chloride = 1.18 grams; ratio = 0.91. Toluene = 20 c.c.  $\alpha = 35.4$ .

| $T$ . | $\alpha$ . | $K_1 \times 10^4$ . | $K_2 \times 10^5$ . | $K_2' \times 10^5$ . |
|-------|------------|---------------------|---------------------|----------------------|
| 2     | 6.1        | 955                 | 292                 | $(T = T - .9)$       |
| 4     | 8.0        | 640                 | 205                 | $\alpha = 23.8$      |
| 9     | 11.45      | 440                 | 150                 | —                    |
| 12    | 12.95      | 370                 | 137                 | 94.2                 |
| 15    | 14.3       | 340                 | 127                 | 93.3                 |
| 18    | 15.45      | 320                 | 121                 | 94.0                 |
| 28    | 18.35      | 260                 | 107                 | 91.5                 |
| 35    | 20.0       | 254                 | 110                 | 91.0                 |
| 42    | 21.3       | 218                 | 103                 | 89.0                 |
| 79    | 25.9       | 166                 | 96                  | 92.0                 |
| 94    | 27.0       | 143                 | 96                  | 92.5                 |
| 109   | 28.0       | 140                 | 97                  | 94.6                 |
| 124   | 28.7       | 134                 | 96                  | 94.6                 |
| 184   | 30.7       | —                   | 96                  | 100.0                |

*Experiment 12.*

Ferric chloride = 1.32 grams. Benzoyl chloride = 1.18 grams; ratio = 1.0. Toluene = 20 c.c.  $\alpha = 35.4$ .

| $T$ . | $\alpha$ . | $K_1 \times 10^4$ . | $K_2 \times 10^5$ . | $K_2' \times 10^5$ . |
|-------|------------|---------------------|---------------------|----------------------|
| 2     | 6.2        | 950                 | 220                 | $(T' = T - 4)$       |
| 4     | 8.4        | 675                 | 168                 | $(\alpha' = 26.9)$   |
| 7     | 10.4       | 500                 | 154                 | —                    |
| 9     | 11.6       | 442                 | 138                 | 100.5                |
| 12    | 13.1       | 367                 | 131                 | 98.5                 |
| 15    | 14.5       | 353                 | 126                 | 98.7                 |
| 18    | 15.7       | 327                 | 116                 | 98.7                 |
| 25    | 18.9       | 279                 | 111                 | 98.8                 |
| 43    | 22.2       | 233                 | 109                 | 100.5                |
| 55    | 24.0       | 207                 | 108                 | 101.0                |
| 73    | 26.0       | 179                 | 111                 | 102.0                |
| 88    | 27.4       | 168                 | 116                 | 106.0                |
| 104   | 28.6       | 157                 | 122                 | 111.0                |
| 125   | 29.8       | 148                 | 135                 | —                    |
| 146   | 30.9       | 141                 | —                   | 134.0                |
| 170   | 31.8       | 134                 | —                   | —                    |

Two other experiments, Nos. 13 and 14, may be briefly summarised.

*Experiment 13.*—Ratio of ferric chloride to benzoyl chloride = 0.46. 25.5 c.c. alkali were neutralised in 1397 minutes. The hydrogen equivalent of ferric chloride used = 16.3 c.c.

The object of this experiment was to ascertain the relationship between the amount of ferric chloride used and ketone formed as measured by the hydrogen chloride evolved. It is noticeable that no such simple relation holds as was found in the case of aluminium chloride.

*Experiment 14.*—Ratio of ferric chloride to benzoyl chloride = 1.8.

$$K_1 = \frac{1}{T} \log \frac{a}{a-x} \text{ varies steadily from } 0.061 \text{ to } 0.011.$$

$$K_2 = \frac{1}{T} \cdot \frac{x}{a(a-x)} \quad " \quad " \quad " \quad 0.00185 \text{ to } 0.00062.$$

From the results of this experiment, taken in conjunction with experiments 11 and 12, it is probable that the reaction, which is apparently bimolecular, is one in which two different molecular species interact; for such a reaction, the following equation holds:

$$K_2 = \frac{1}{(a-b)T} \cdot \log \frac{a(b-x)}{b(a-x)},$$

where  $a$  and  $b$  represent the initial concentrations of the reacting substances. For the special case that  $a=b$ , this takes the form used

above,  $K_2 = \frac{1}{T} \cdot \frac{x}{a(a-x)}.$

In experiments 13 and 14, in which apparently  $a$  and  $b$  are not equal, there is no means by which  $b$  can be determined, but by assigning various values to this constant in experiment 14, it has been found that the reaction is bimolecular if  $b=44.2$ . This will be seen from the following figures:

*Experiment 15.*—If  $a=27.2$  and  $b=44.2$ ,  $K_2 = \frac{1}{(b-a)T} \log \frac{a(b-x)}{b(a-x)}$

|                     |   |    |    |      |    |     |     |
|---------------------|---|----|----|------|----|-----|-----|
| $T$                 | = | 4  | 14 | 26   | 51 | 121 | 178 |
| $K_2 \times 10^5 =$ |   | 43 | 36 | 35.4 | 31 | 32  | 35  |

This appears to indicate that in addition to the substance  $\text{FeCl}_6(\text{C}_6\text{H}_5\cdot\text{COCl})_2$  there is present a second compound of ferric chloride and toluene, the concentration of which varies with the amount of ferric chloride present, and in the synthesis of ketones from hydrocarbon and acid chloride by the aid of this reagent, the reaction which occurs between these compounds comes to a standstill from the

fact that the ferric chloride is withdrawn from the system as a component of the final product. This ketonic compound is, however, not so stable as the analogous one containing aluminium chloride.

### *Hydrocarbon Synthesis.*

#### *(a) The Reaction between Benzoyl Chloride and Toluene in the presence of Aluminium Chloride.*

All the experiments in this series were made with the same mixture of benzyl chloride and toluene, namely, one in which 0.434 gram of benzyl chloride is contained in 30 c.c. of toluene.

With stronger solutions and with quantities of aluminium chloride greater than 0.02 gram, the rate of this reaction cannot be satisfactorily measured on account of its rapidity.

TABLE VII.

#### *Experiment 16.*

Aluminium chloride = 0.004 gram.  
HCl evolved 2.5 c.c.  $A = 2.5$ .

| $T.$ | $x.$ | $K_1 \times 10^4.$ |
|------|------|--------------------|
| 1.15 | 1.0  | 445                |
| 2.0  | 1.75 | 600                |
| 3.0  | 2.1  | 611                |
| 5.0  | 2.3  | 510                |
| 8.5  | 2.45 | 460                |

\*  $R = 20$ .

#### *Experiment 17.*

Aluminium chloride = 0.010 gram.  
HCl evolved 7.9 c.c.  $a = 7.9$ .

| $T.$ | $x.$ | $K_1 \times 10^4.$ |
|------|------|--------------------|
| 1.3  | 2.0  | 2305               |
| 1.8  | 2.8  | 2420               |
| 2.6  | 3.9  | 2600               |
| 3.15 | 4.5  | 2670               |
| 3.8  | 5.1  | 2720               |
| 4.7  | 5.6  | 2630               |
| 5.7  | 6.1  | 2600               |
| 6.8  | 6.6  | 2650               |
| 8.15 | 7.0  | 2670               |
| 11.0 | 7.4  | 2520               |
| 15.0 | 7.6  | 2180               |
| 40.0 | 7.9  | —                  |

\*  $R = 25$ .

#### *Experiment 18.*

Aluminium chloride = 0.011 gram.

HCl evolved 8.55 c.c.

| $T.$ | $x.$ | $K_1 \times 10^4.$ | $T.$ | $x.$ | $K_1 \times 10^4.$ |
|------|------|--------------------|------|------|--------------------|
| 1.60 | 5.0  | 5480               | 4.0  | 7.5  | 5250               |
| 2.15 | 6.0  | 5620               | 5.33 | 7.8  | 4620               |
| 2.6  | 6.5  | 5480               | 8.5  | 8.1  | 3460               |
| 3.1  | 6.9  | 5300               | 27.0 | 8.55 | —                  |

\*  $R = 24.5$ .

\*  $R$  = ratio of benzoyl chloride decomposed to aluminium chloride.



Table VII contains the details of three experiments carried out with varying quantities of aluminium chloride. From these, it is seen that the reaction is unimolecular, and comes to a standstill at a perfectly definite point, namely, when for every gram equivalent of aluminium chloride added, twenty-five molecules have entered into reaction. Other experiments were made with still smaller quantities of aluminium chloride, and as an invariable rule it has been noticed that the evolution of hydrogen chloride never occurred unless an intense orange colour developed in the reaction mixture, which disappeared almost entirely as the evolution came to an end.

This colour is probably due to the formation of a compound of aluminium and benzyl chlorides. The cessation of the reaction at a definite point is easily understood if the existence is assumed of a dissociable compound of the hydrocarbon produced and the aluminium chloride, the substance dissociating according to the equation :



For, if  $a$ ,  $b$ , and  $c$  represent the concentration of the compound, the aluminium chloride, and the hydrocarbon respectively, equilibrium is established when  $\frac{bc^2}{a} = \text{a constant}$ , and therefore as  $c$  is increased, a value will ultimately be reached for  $b$ , so small that for all practical purposes the concentration of the aluminium chloride will be zero. It can therefore exert no further influence on the reaction, which accordingly either ceases or becomes immeasurably slight, a condition which is fulfilled in the present case when  $c = 250$ .

This synthesis may therefore be regarded as analogous to that of the ketone, from which it differs only in the greater instability of the final aluminium chloride compound.

*The Reaction between Benzyl Chloride and Toluene in the presence of Ferric Chloride.*

The reaction mixture was the same as that used in the last series.

The details of four experiments, in which the quantities of ferric chloride varied from 0.54 to 0.004 gram, are given in Table VIII.

TABLE VIII.

*Experiment 19.*

Ferric chloride = 0.53 gram ; ratio of ferric chloride to benzyl chloride  
= 1.05.  $\alpha = 14.5$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 2.15  | 9.3   | 478                 | —                    | —       |
| 2.75  | 10.9  | 496                 | —                    | —       |
| 3.25  | 11.2  | 446                 | —                    | —       |
| 3.9   | 11.8  | 431                 | —                    | —       |
| 4.6   | 12.4  | 423                 | —                    | —       |
| 5.7   | 13.2  | 424                 | —                    | —       |
| 6.5   | 13.5  | 414                 | —                    | —       |
| 7.25  | 13.7  | 403                 | —                    | —       |
| 9.0   | 14.1  | 403                 | —                    | —       |
| 10.0  | 14.2  | 386                 | —                    | —       |

*Experiment 20.*

Ferric chloride = 0.038 gram ; ratio = 0.068.  $\alpha = 14.5$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 1.0   | 2.0   | 147                 | —                    | 2.0     |
| 1.5   | 5.1   | 276                 | —                    | 3.4     |
| 2.0   | 8.0   | 403                 | —                    | 4.0     |
| 2.5   | 10.6  | 526                 | —                    | 4.25    |
| 3.0   | 12.5  | 661                 | —                    | 4.16    |
| 4.0   | 13.4  | 646                 | —                    | 3.35    |
| 4.5   | 13.8  | 672                 | —                    | —       |
| 5.75  | 14.0  | 590                 | —                    | —       |

*Experiment 21.*

Ferric chloride = 0.018 gram. Ratio = 0.032.  $\alpha = 14.5$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 3.5   | 4.4   | 104                 | $(T' = T - 5)$       | 1.25    |
| 4.0   | 5.5   | 115                 | $(\alpha' = 7.1)$    | 1.37    |
| 5.0   | 7.6   | 139                 |                      | 1.50    |
| 6.0   | 9.7   | 184                 | 391                  | 1.60    |
| 7.0   | 11.3  | 216                 | 400                  | 1.61    |
| 8.0   | 12.4  | 241                 | 405                  | 1.55    |
| 9.0   | 13.1  | 260                 | 405                  | 1.44    |
| 10.0  | 13.45 | 262                 | 394                  | —       |
| 11.0  | 13.75 | 262                 | 380                  | —       |

*Experiment 22.*

Ferric chloride = 0.004 gram ; ratio = 0.0071.  $a = 14.5$ .

| $T$ . | $x$ . | $K_1 \times 10^3$ . | $K_1' \times 10^3$ . | $x/T$ . |
|-------|-------|---------------------|----------------------|---------|
| 11.5. | 5.15  | 37.3                | $(T'' = T - 11.5)$   | 0.447   |
| 16.15 | 9.8   | 69.7                | $(a' = 9.4)$         | 0.607   |
| 17.0  | 10.7  | 78.6                | 165                  | 0.603   |
| 18.0  | 11.3  | 84.0                | 167                  | 0.627   |
| 19.0  | 11.9  | 90.5                | 171                  | 0.627   |
| 20.0  | 12.3  | 94.4                | 170                  | 0.615   |
| 21.0  | 12.8  | 102.0               | 180                  | 0.610   |
| 23.0  | 13.3  | 112.0               | 179                  | 0.578   |
| 26.0  | 13.9  | 122.0               | 190                  | —       |
| 33.0  | 14.1  | —                   | —                    | —       |

In all the above experiments, with the exception of No. 19, in which some disturbing cause may be suspected which diminishes the value of  $K_1$ , the phenomenon of chemical induction can be detected, and to a very much greater extent in those in which the amount of ferric chloride is small. This may be accounted for by the slower rate at which the compound of benzyl chloride and ferric chloride is formed when the quantity, and thus the surface of contact of the latter with the solution, is small. Apart from this effect, the reaction is unimolecular.

There is no indication of the occurrence of any compound between the ferric chloride and the hydrocarbon produced in this reaction, in which the ferric chloride appears to behave as a true catalytic agent.

*Summary.*

The dynamical study of the four foregoing reactions leads to the following conclusions :

(1) In the synthesis of ketones from hydrocarbon and acid chloride in the presence of aluminium chloride, the reaction is unimolecular, and the mechanism, suggested by Perrier and Boeseken, is well established, provided the ratio of aluminium chloride to acid chloride is not greater than unity.

(2) In the presence of an excess of aluminium chloride, the reaction is best explained as being bimolecular, the reacting species being two intermediate compounds, each containing aluminium chloride.

(3) In the presence of ferric chloride, the reaction between the same classes of substance is bimolecular, and is best explained in the same manner as the foregoing condensation (2).

(4) In the synthesis of phenyltolylmethane from toluene and



benzyl chloride in the presence of aluminium chloride, the reaction is unimolecular, and is probably one between toluene and a compound of aluminium and benzyl chlorides, and the same applies to the reaction in the presence of ferric chloride.

In the first three of the above reactions, the action ceases at a point when all the metallic chloride is withdrawn from the system as a component of the final product. In the last reaction, no evidence of this can be found, and the ferric chloride acts as a true catalyst. Hence it may be stated that the action of aluminium and ferric chlorides in inducing the Friedel-Crafts reaction differs from many cases of true catalysis only in the accident that these reagents combine with certain substances produced during the reaction and are thus removed from the system.

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# ERRATA.

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| Page | Line |                        |
|------|------|------------------------|
| 641  | 5    | for "0·2" read "0·02." |
| 649  | 1    | „ "8·7" read "9·7."    |

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|      |              |   |
|------|--------------|---|
| 112  | 3            | for "solubility" read "insolubility."   |
| 188  | 5 and 6      | „ "mm." read "milligram."   |
| 284  | 2            | „ $\text{C}_6\text{H}_5\cdot\overset{\textstyle  }{\text{C}}-\overset{\textstyle  }{\text{CH}}\cdot\overset{\textstyle  }{\text{CH}}$ read $\text{C}_6\text{H}_5\cdot\overset{\textstyle  }{\text{C}}-\overset{\textstyle  }{\text{CH}}\cdot\text{CH}_3$ ." |
| 298  | 2            | „ "The sparingly soluble potassium salt" read "A small quantity of the potassium salt."   |
| 298  | 2*           | delete Footnote.  |
| 309  | 3            | for "dimethyloxidoglutamic acid" read "dimethyldiphenyloxido-glutaric acid."  |
| 654  | 8            | „ "R. U. HUMMEL" read "ROBERTS BEAUMONT."   |
| 788  | (footnote) 1 | add "(Proc. Roy. Soc., 1902, 70, 153)."   |
| 1397 | 20           | for "1902" read "1903."   |
| 1413 | 20           | „ "H=6·9; N=7·3" read "H=7·3; N=4·9."   |

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